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④ A method for manufacturing titanium oxide.

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⑯ References cited: <b>EP-A- 0 298 763 EP-A- 0 301 700 US-A- 3 104 950</b>  <b>CHEMICAL ABSTRACTS, vol. 76, no. 24, 12th June 1972, page 125, abstract no.142955h, Columbus, Ohio, US; V.A. BLASHUK et al.: "Extraction of titanium(IV)sulfate acidic complexes by primary amines"</b>	⑦ Representative: <b>Gillam, Francis Cyril et al SANDERSON &amp; CO. European Patent Attorneys 34, East Stockwell Street Colchester Essex CO1 1ST (GB)</b>

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**CHEMICAL ABSTRACTS**, vol. 90, no. 22, May 1979, page 350, abstract no. 174062v, Columbus, Ohio, US; YU.V. FILATOV et al.: "Study of the possibility of extractive regeneration of sulfuric acid which is a waste from titanium dioxide production. Communication II. Extraction of titanium from sulfuric acid solutions with some organic solvents", & TR., NAUCHNO-ISSLED. INST. UDOBR. INSEKTOFUNGITS. 1976, 227, 53-4

**PATENT ABSTRACTS OF JAPAN**, vol. 6, no. 177 (C-124)[1055], 11th September 1982; & JP-A-57 92 194 (NIHON KEIKINZOKU K.K.) 08-06-1982

**Description**

The present invention relates to a method for manufacturing titanium oxide.

In the manufacture of titanium oxide by a known sulfuric acid process, a titanium-iron-containing substance such as a titanium-iron ore (limenite, or anatase) and titanium slag is brought into contact with concentrated sulfuric acid at an elevated temperature to produce a solid product composed mainly of a sulfated product of titanium containing ferrous sulfate, ferric sulfate, and titanyl sulfate as the main constituents together with magnesium sulfate, chromium sulfate, manganese sulfate, vanadium sulfate, sulfates of other elements, and unreacted substances. The solid is subsequently put into water or sulfuric acid solution for leaching, and then a reducing agent such as iron scrap is added to convert the ferric sulfate to ferrous sulfate. The solution is cooled to precipitate ferrous sulfate crystal ( $FeSO_4 \cdot 7H_2O$ ), giving a titanium-iron solution containing titanyl sulfate in which the iron content is decreased. The titanyl sulfate is hydrolyzed in such a manner that the concentrated titanyl sulfate solution is gradually added into a dilute titanyl sulfate solution at a near boiling state to raise the concentration of titanyl-iron sulfate and then water heated to 90 - 95 °C is added thereto in an amount of 1/4 in volume relative to the titanyl sulfate solution.

This method is disadvantageous in that as much as 5 - 6 % of the titanyl sulfate remains in the solution without converting to titanium hydroxide and is discarded even though the total sulfuric acid concentration in the hydrolyzed aqueous solution is 350 - 400 g/l  $H_2SO_4$ , while 94 % to 95 % of the titanyl sulfate precipitates as a hydroxide.

A solvent extraction technology for titanium oxide manufacture is disclosed in USP 3,067,010. This technology relates to a selective extraction of a titanium ion species from the sulfuric acid solution by contact with an organic solvent containing an alkylphosphoric acid to separate titanium from iron in titanyl-iron sulfate in the sulfuric acid solution. This method is disadvantageous in that the iron is co-extracted in a large amount and that the 5-6N HCl used for removal of the iron, and HF and  $NH_3$  for inverse extraction of Ti from the organic phase are less economical in comparison with the conventional methods of hydrolysis for titanium hydroxide manufacture.

Methods for separating titanium ions and iron ions contained in a chloride solutions are disclosed in USP 3,795,727 and USP 3,104,950. Both methods relate to extraction of iron chloride complex from an aqueous solution, and have many disadvantages such that the total HCl concentration in the aqueous solution employed has to be sufficiently high, so that the extracting agents are significantly soluble in the aqueous solution, and that the titanium is coexisting with impurity metal ions other than iron, which requires further purification.

A further method was presented at the meeting of the Metallurgical Society of AIME held on February, 16-20, 1969, regarding selective removal of Cr (III) ions by extraction, by use of a primary amine, from a waste sulfuric acid solution containing Ti ions and Cr (III) ions for the purpose of recycling the sulfuric acid. Still further, a method is described regarding selective removal of Cr (VI) ions from a sulfuric acid solution containing Ti ions and Cr ions by use of a tertiary or quaternary alkylamine in Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, No. 3, 1970. Both methods, however, relate to extraction of Cr ions and Nb ions as impurities in a form of a sulphate complex without extracting Ti ions in the sulfuric acid solution and with Ti ions kept in the aqueous solution. Accordingly, these methods are different in principle from the present invention in which Ti ion is extracted and is further purified.

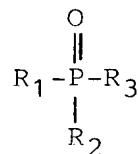
The disadvantages of prior art mentioned above are eliminated in the present invention, as defined hereinafter, by extraction of titanium-sulfate complex with an organic solvent, inverse extraction of titanium from the organic solvent with water or a dilute aqueous sulfuric acid solution, and recycling of the resulting aqueous solution to hydrolysis or leaching of the titanyl sulfate. Such a method according to the present invention allows prevention of loss of titanium oxide unrecovered in the hydrolyzed solution and the potential causing of pollution problems. Thus, the titanyl sulfate is totally converted to titanium hydroxide and then fired into titanium oxide.

The efficiency of the inverse extraction may be improved by adding a reducing agent into the water or the dilute aqueous sulfuric acid solution employed for the inverse extraction of titanium from the organic solvent. Otherwise, the efficiency of the inverse extraction may be improved by bringing the organic solvent into contact with a reducing agent prior to the inverse extraction and then conducting inverse extractions of titanium from the organic phase into water or a dilute aqueous sulfuric acid solution. Since water balance can be maintained well even when the aqueous solution is recycled repeatedly, the dissolved titanyl in the (aqueous) solution separated after the hydrolysis can be converted totally to titanium hydroxide: in other words, all the titanium contained in the starting titanyl-iron sulfate solution may be recovered as titanium hydroxide.

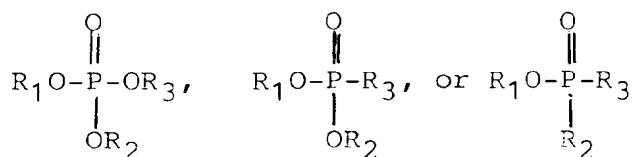
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According to an aspect of the present invention, there is provided a method for manufacturing titanium oxide from an aqueous sulfuric acid solution containing predominantly titanium ions and one or more other metal ions, which includes the steps of:

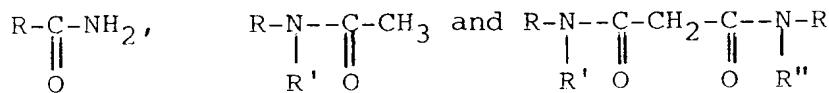
5 a. subjecting said solution to hydrolysis to form insoluble titanium hydroxide;  
b. separating the insoluble titanium hydroxide thus formed from the residual aqueous solution;  
c. contacting the separated aqueous solution with a water-immiscible organic solvent consisting of or  
containing one or more oxygen-containing organic solvents, alkyl amines and/or alkyl aryl amines  
selected from:  
10 (i) a secondary amine represented by the general formula  $R_2NH$  where  $R$  is an alkyl or aryl radical  
having from 4 to 24 carbon atoms; and/or  
(ii) a trialkylphosphine oxide represented by the general formula:



20 (wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, which may be the same or different, each represents an alkyl or aryl radical having from 4 to 18 carbon atoms); and/or  
(iii) a neutral alkyl phosphoric ester of general formula:



(wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, have the same meaning as above); and/or  
35 (iv) a primary, secondary or tertiary alcohol having from 6 to 18 carbon atoms; and/or  
(v) an amide of general formula:



(wherein R, R' and R", which may be the same or different, each represents an alkyl or an aryl radical having from 4 to 22 carbon atoms);  
so as thereby to extract still-dissolved titanium ions in the form of a sulfate titanyl complex into the organic solvent, and thereafter separating the resultant organic solvent extract from the aqueous raffinate;  
45 d. contacting the separated organic solvent extract with water or dilute aqueous sulfuric acid solution to re-extract the titanium therefrom into the water or dilute aqueous sulfuric acid solution, thereby regenerating the organic solvent;  
50 e. recycling the titanium-containing aqueous solution containing the re-extracted titanium back to hydrolysis step a.; and  
f. calcining the separated titanium hydroxide from step b. to produce titanium oxide.

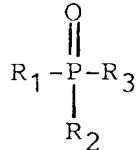
According to another aspect of the present invention, there is provided a method for manufacturing titanium oxide from an aqueous sulfuric acid solution containing predominantly titanium ions and one or more other metal ions, which includes the steps of:

55 a. subjecting said solution to hydrolysis to form insoluble titanium hydroxide;  
b. separating the insoluble titanium hydroxide thus formed from the residual aqueous solution;  
c. contacting the separated aqueous solution with a water-immiscible organic solvent consisting of or containing one or more oxygen-containing organic solvents, alkyl amines and/or alkyl aryl amines

selected from:

(i) a secondary amine represented by the general formula  $R_2NH$  where  $R$  is an alkyl or aryl radical having from 4 to 24 carbon atoms; and/or  
 (ii) a trialkylphosphine oxide represented by the general formula:

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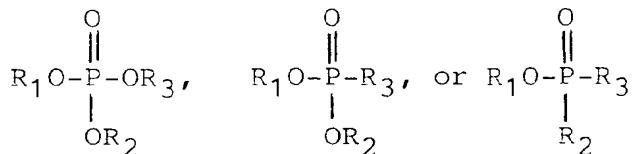
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(wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, each represents an alkyl or aryl radical having from 4 to 18 carbon atoms); and/or

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(iii) a neutral alkyl phosphoric ester of general formula:

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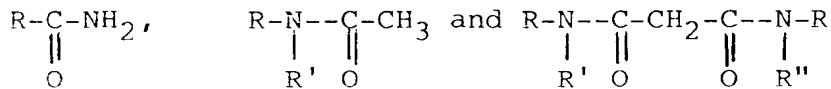
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(wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, have the same meaning as above); and/or

(iv) a primary, secondary or tertiary alcohol having from 6 to 18 carbon atoms; and/or

(v) an amide of general formula:

30



35

(wherein  $R$ ,  $R'$  and  $R''$ , which may be the same or different, each represents an alkyl or an aryl radical having from 4 to 22 carbon atoms);

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so as thereby to extract still-dissolved titanium ions in the form of a sulfate titanyl complex into the organic solvent, and thereafter separating the resultant organic solvent extract from the aqueous raffinate; d. contacting the separated organic solvent extract with water or dilute aqueous sulfuric acid solution to re-extract the titanium therefrom into the water or dilute aqueous sulfuric acid solution, thereby regenerating the organic solvent;

e. recycling the titanium-containing aqueous solution containing the re-extracted titanium back to hydrolysis step a.; and

f. calcining the separated titanium hydroxide from step b. to produce titanium oxide; and a second step of adding, to the aqueous raffinate resulting from the first step, at least one compound selected from the group of chlorides of Na, K, Mg, Ca, and/or  $NH_4$  in an amount equivalent chemically to the sum of free  $SO_4$  ions in the raffinate, and subsequently bringing said raffinate into contact with a second organic solvent (B) containing one or more of the species selected from the previously-defined oxygen-containing organic solvents, alkyl amines and alkyl aryl amines to extract iron ions as a chloride complex from the raffinate into the second organic solvent (B); and thereafter bringing the second organic solvent (B) containing iron ions and chloride ions into contact with water inversely to extract the iron ions and the chloride ions from the second organic solvent into the water and to regenerate the second organic solvent (B).

According to still another aspect of the present invention, there is provided a method for manufacturing titanium oxide, comprising bringing a sulfuric acid solution containing predominantly titanium ions and additionally one or more metal ions including iron ions into contact with an organic solvent containing one or more of the species selected from the previously-defined oxygen-containing organic solvents, alkyl amines, and alkyl aryl amines, and thereafter introducing the sulfuric acid solution to an evaporation-concentration step operated at a reduced or normal pressure to recover concentrated sulfuric acid, thus decreasing the

quantity of the sulfated titanium formed at the evaporation-concentration step.

According to a further aspect of the present invention, there is provided a method for manufacturing titanium oxide, comprising adding, to a sulfuric acid solution containing predominantly titanium and additionally one or more of iron and other metal ions, at least one species selected from the chlorides of H, 5 Na, Mg, K, Ca, and NH<sub>4</sub> in an amount of addition required to form a chloride complex of the titanium ion in the sulfuric acid solution, thereafter bringing the sulfuric acid solution into contact with an organic solvent containing at least one species selected from the previously-defined oxygen containing organic solvents, alkyl amines, and alkyl aryl amines to extract the titanium from the sulfuric acid solution in a form of a chloride complex, and subsequently bringing the organic solvent containing titanium ions and chloride ions 10 into contact with water inversely to extract the titanium ions and the chloride ions from the organic solvent into the water and to regenerate the organic solvent.

The above aspects of the invention are described below in relation to the accompanying drawings of which a brief description is as follows:

Fig. 1 is a flow sheet illustrating the prototype of the present invention;  
 15 Fig. 2 shows a modification made by attaching an operation of adding a reducing agent to water or an aqueous dilute sulfuric acid solution for inverse extraction to improve the efficiency of inverse extraction of titanium from the organic phase.  
 Fig. 3 shows another modification made by an additional step of bringing the titanium into contact with a reducing agent before the titanium in an organic phase is introduced to an inverse extraction step to 20 improve the inverse extraction efficiency.  
 Fig. 4 is a flow sheet illustrating a further modification of the process. In this process, water or an inverse extraction liquid containing titanium is added to a titanyl-iron sulfate solution in a hydrolysis step to precipitate most portion of the titanium from the sulfuric solution in the form of insoluble titanium hydroxide. The titanium remaining in the filtrate is extracted (by an organic solvent) as a sulfuric acid 25 complex. The organic solvent containing the extracted titanium is led to an inverse extraction step to come into contact with water or an aqueous dilute sulfuric acid solution, whereby the titanium is inversely extracted from the organic solvent to the aqueous solution which is recycled to hydrolysis.  
 Fig. 5 is a process resulting from a combination of Fig. 3 and Fig. 4.  
 Fig. 6 illustrates a subsequent process added to the process of Fig. 4, where rock salt is added to the 30 raffinate and the mixture is oxidized to change the iron ion in the raffinate to chlorides, and then the iron ion complex with chlorides is extracted and neutralized.  
 Fig. 7 illustrates an effect of the present invention in concentration and recovery of the sulfuric acid solution after extractive removal of titanium subsequent to the process of Fig. 4.  
 Fig. 8 illustrates a process of titanium hydroxide recovery where titanium recovery liquid is heated and 35 subjected to hydrolysis to recover titanium hydroxide, and the solution is then recycled to a process similar to that of Fig. 4 or Fig. 7.  
 Fig. 9 is fundamentally similar to Fig. 7. In Fig. 9, the (aqueous) solution from which the titanium has been removed by extraction (with the organic solvent) is concentrated, and the resulting concentrated sulfuric acid is recycled.  
 40 Fig. 10 is fundamentally similar to Fig. 8. In Fig. 10, an alkali is added to the aqueous solution which contains titanium recovered by inverse extraction to recover titanium hydroxide.  
 Fig. 11 illustrates a method for recovering titanium hydroxide. In Fig. 11, the titanyl-iron sulfate solution is subjected to hydrolysis. The insoluble titanium hydroxide formed is removed off. To the sulfuric acid 45 solution, a substance is added which is selected from the compounds of Na and Cl; Mg and Cl; NH<sub>4</sub> and Cl; K and Cl and Ca and Cl; and HC1. Thereafter titanium is extracted as a chloride complex. The organic solvent containing the extracted titanium is brought into contact with water, whereby titanium is inversely extracted from the organic phase to the aqueous phase. To the resulting aqueous solution containing recovered titanium, an alkali is added to recover titanium hydroxide. The method for neutralization treatment of the sulfuric acid after extractive removal of titanium is conducted in the same 50 manner as in Fig. 6.

The invention will now be described in its preferred aspects, after which it will be illustrated by way of example with reference to the accompanying drawings.

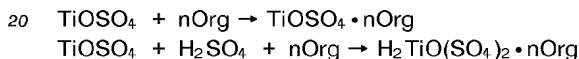
Any titanyl iron sulfate solution may be used in the present invention as a starting material regardless of the preparation method of the present invention selected from the above aspects. Conventionally employed 55 titanium and iron sulfate solution is prepared through the steps of finely pulverizing titanium-iron ore (ilmenite or anatase) or titanium-concentrated material such as titanium ore slag, agitating it with concentrated sulfuric acid to cause ageing at a high temperature, leaching it with water or dilute sulfuric acid, adding iron scrap to reduce ferric sulfate to ferrous sulfate, cooling the solution to remove iron sulfate

( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), and removing solid matter.

An example of a titanium iron solution contains 240 - 260 g/l of  $\text{TiO}_2$ , 40 - 50 g/l of  $\text{Fe}^{2+}$ , 200 - 300 g/l of free sulfuric acid, 500 - 800 g/l of total sulfuric acid, and metal irons of Mn, V, Mg, Al, Cr, and Nb.

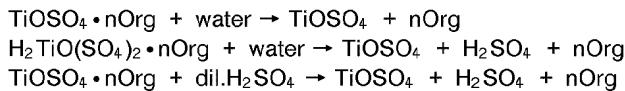
Insoluble titanium hydroxide is prepared from titanium-iron solution by hydrolysis by various methods including those disclosed by USP 2,253,595 and British Patent 558,285. Generally, the insoluble titanium hydroxide is prepared by gradually adding titanium iron solution of a high concentration obtained through leaching the raw material into a low concentration solution of titanyl sulfate at a boiling state to form a concentrated titanyl sulfate-iron solution, and adding, to the titanium-iron solution kept at 95 - 105 °C approximately 1/4 an amount by volume of water maintained at 90 - 95 °C relative to the titanium-iron solution. On completion of the hydrolysis, the total sulfuric acid concentration in the solution is in the range of from 320 - 450 g/l, and the titanium ion remaining unhydrolyzed in the water solution is in the range of from 7 - 10 g/l as  $\text{TiO}_2$ , which means that 94 - 95 % of the total titanyl sulfate is converted to titanium hydroxide.

In the present invention, the Ti ion remaining in the hydrolyzed solution is extracted by contact with an organic solvent containing one or more of the species selected from the previously-defined oxygen-containing organic solvents, alkyl amines, and alkyl aryl amines, whereby the titanium ion in the sulfuric acid solution is extracted into the organic phase as a complex shown in the formulas below as an example, being separated from other metals.

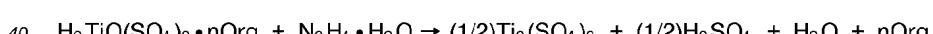


The above formulas show only examples of the extraction reaction. It should be understood that the reaction depends on the concentration of  $\text{SO}_4$  in the aqueous solution, the concentration of the co-existing metal ions and the kind of existing anion, and that the chemical species of the titanium extracted depends on the extracting agent employed.

30 The sulfuric acid complex of titanium extracted into an organic solvent containing a species selected from the previously-defined oxygen-containing organic solvents, alkyl amines and alkyl aryl amines is transferred to an aqueous phase when the complex is brought into contact with water or a dilute sulfuric acid as shown for example in the formulas below, and the organic solvent is regenerated.



35 Hydrazine, hydrazine sulfate,  $\text{Na}_2\text{SO}_3$ ,  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $(\text{COOH})_2$ , and ascorbic acid, or the like, when added to the water of the dilute sulfuric solution for the inverse extraction, will increase the efficiency of the inverse extraction, and will allow the recovery of titanium in a high concentration:



The above formula shows only an example of the reaction in the inverse extraction. The titanium ion is not always entirely converted to  $\text{Ti}^{3+}$  ion because the conversion depends on the amount of the reducing agent. A very small amount of titanium may remain un-reduced, or it may, after transfer to the aqueous phase, be 45 re-oxidized to  $\text{Ti}^{4+}$  ion.

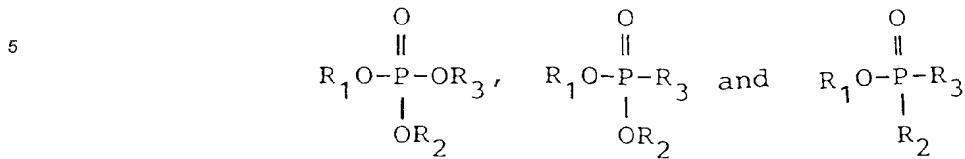
Further it should be understood that the state of titanium species will depend upon the contact condition of the organic phase with the reducing agent before the inverse extraction and upon the kind of the extracting agent employed.

50 The solution containing the inversely-extracted titanium having a low concentration of sulfuric acid is recycled repeatedly either for hydrolysis of titanyl sulfate solution or for leaching the solid titanyl sulfate resulting from the reaction of titanium-iron ore with concentrated sulfuric acid, and thus the titanium is recovered as titanium hydroxide.

The aqueous solution containing inversely-extracted titanium can also be used for preparation of titanium hydroxide by addition of an alkali thereto since the solution contains no other metallic ion.

55 The oxygen-containing organic solvent employed in the present invention may be selected from the following:

(a) Neutral alkyl phosphoric esters:

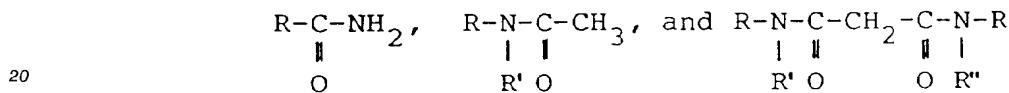


10 wherein  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  represent alkyl radicals and aryl radicals having 4 to 18 carbons, including cases where the alkyl radicals or the aryl radicals differ from each other or alkyl and aryl radicals are mixedly employed, namely  $\text{R}_1 = \text{R}_2 = \text{R}_3$ ,  $\text{R}_1 = \text{R}_2 \neq \text{R}_3$ , or  $\text{R}_1 \neq \text{R}_2 \neq \text{R}_3$ .

(b) Alcohols:

15 Primary, secondary, and tertiary alcohols having 6 to 18 carbon atoms.

(c) Amides:



25 wherein  $\text{R}$ ,  $\text{R}'$ , and  $\text{R}''$  represent respectively an alkyl radical or an aryl radical having 4 to 22 carbons, including cases where the radicals differ from each other or alkyl and aryl radicals are mixedly employed, namely  $\text{R} = \text{R}' = \text{R}''$ ,  $\text{R} = \text{R}' \neq \text{R}''$ , or  $\text{R} \neq \text{R}' \neq \text{R}''$ .

(d) Trialkyl phosphine oxides:

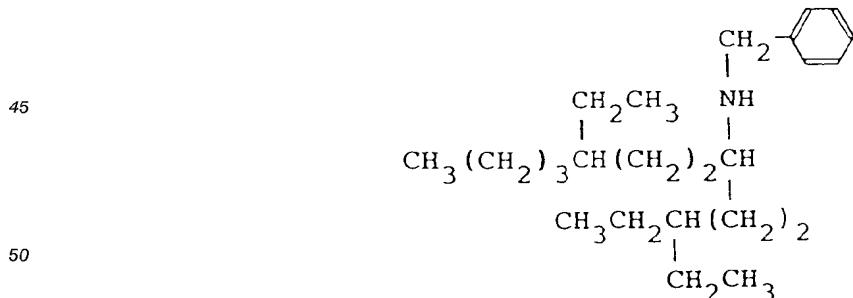


35 (wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$ , which may be the same or different, each represents an alkyl or aryl radical having from 4 to 18 carbon atoms).

The alkyl amines and alkyl aryl amines employed in the present invention may be selected from secondary amines represented by  $\text{R}_2\text{NH}$  where  $\text{R}$  is an alkyl or aryl radical having 4 to 24 carbons.

An example is as shown below:

40



55 Petroleum hydrocarbons used for dilution of the extracting agent in the present invention include aromatic hydrocarbons, aliphatic hydrocarbons and a mixture thereof. Kerosine, a mixture of various hydrocarbons, is frequently used.

The typical compound containing Na and Cl employed in the present invention is rock salt (NaCl) the purity of which is not limited.  $\text{NaClO}_x$  may also be employed. Further, seawater or an industrial waste may

naturally be employed also.

The compounds containing Ca and Cl; Na and SO<sub>4</sub>; NH<sub>4</sub> and Cl; NH<sub>4</sub> and SO<sub>4</sub>; K and Cl; or K and SO<sub>4</sub> may be obtained from industrial waste which are exhausted in large quantities, irrespectively of the purity thereof.

5 The compound containing Mg and Cl, or Mg and SO<sub>4</sub> in the present invention may be used also irrespectively of the purity thereof.

The reducing agent employed in the present invention is a species or a mixture of two or more thereof such as H<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, Na<sub>2</sub>S, NaHS, NaC<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>C<sub>2</sub>O<sub>4</sub>, CH<sub>3</sub>COOH, CH<sub>3</sub>COONH<sub>4</sub>, CH<sub>3</sub>COONa, NaHSO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>HSO<sub>3</sub>, KHSO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, metallic iron, 10 metallic zinc, hydrazine hydrate, hydrazine sulfate, citric acid, malic acid, gluconic acid, urea, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, and ascorbic acid.

The dilute sulfuric acid used for inverse extraction in the present invention is in a concentration of not more than 250 g H<sub>2</sub>SO<sub>4</sub> per liter in the case where it is used solely without a reducing agent added, but the concentration may be up to 300 g H<sub>2</sub>SO<sub>4</sub> per liter in the case where the extracting agent is contained in a 15 concentration of not more than 5 %. In the case where a reducing agent is mixed (to the organic solvent) in the inverse extraction, the concentration of the sulfuric acid is not limited specifically.

Specific embodiments of the present invention will now be described in more detail on the basis of the accompanying drawings. The present invention, however, is not limited by the description which follows.

Fig. 1 shows a prototype of the present invention, where a titanyl sulfate solution A containing impurity 20 metal ions is introduced to the step B and is brought into contact with an organic solvent (a) containing an extractant selected from previously-defined oxygen-containing solvents, alkyl amines, and alkyl aryl amines to extract titanyl sulfate from the sulfuric acid solution to an organic phase in the form of a sulfuric acid complex. The organic solvent (a) containing the extracted titanium is transferred to the inverse extraction step C where, in contact with water or dilute aqueous sulfuric acid (b), titanium is inversely extracted into an 25 aqueous solution, and the organic solvent (a) is regenerated and recycled.

The raffinate (c) is subsequently transferred to an acid recovery step or a neutralization step. The liquid (d) after completion of the inverse extraction is led to a hydrolysis step from whence titanium hydroxide is recovered. The titanium hydroxide is fired into titanium dioxide.

Fig. 2 shows a flow sheet similar to Fig. 1. In Fig. 2, for the purpose of improving the efficiency of the 30 inverse extraction, a reducing agent (e) is added to water or a dilute aqueous sulfuric acid solution (b) serving as the inverse extraction liquid at the inverse extraction step C where titanium is extracted to the aqueous phase by contact with the organic solvent (a) containing titanium and entering the inverse extraction step C.

Fig. 3 also shows a flow sheet similar to Fig. 1 and Fig. 2, illustrating a basic process of the present 35 invention. In Fig. 3, the organic solvent (a) containing titanium is, prior to the inverse extraction, led to a reduction step D where the valency of the titanium in the organic phase is changed under the action of a reducing agent (e) added thereto, and subsequently the titanium is brought into contact with water or a dilute aqueous sulfuric acid solution (b) in the inverse extraction step C and is inversely extracted into the aqueous phase, thus improving the efficiency of the inverse extraction.

40 Fig. 4 shows a combination of the process of the present invention with a conventional sulfuric acid process for manufacturing titanium oxide. In Fig. 4, to the titanyl sulfate solution A containing much impurity metal ions and being kept boiling at the hydrolysis step E, water or dilute titanyl sulfate solution (d) is added to form insoluble titanium hydroxide while the total concentration in the titanyl sulfate solution is being lowered. The titanium hydroxide G is separated at a filtration step F from the sulfuric acid solution 45 containing titanium ion as well as other metal ions of Fe, Mn, Al, Cr, V, Mg, Nb, Zn, etc. The filtrate is led to the extraction step B, and brought into contact with an organic solvent (a) containing an extractant selected from the previously-defined oxygen-containing organic solvents, alkyl amines, and alkyl aryl amines to extract the titanium ions from the sulfuric acid solution into an organic phase in the form of sulfuric acid complex. The organic solvent (a) containing the titanium is introduced to an inverse extraction step C and is brought into contact with water or dilute sulfuric acid (b) inversely to extract the titanium into the aqueous solution, and thus the organic solvent (a) is regenerated and recycled. The solution (d) having completed 50 the inverse extraction is introduced to the hydrolysis step E, and the titanium is recovered as titanium hydroxide and fired into titanium oxide.

Fig. 5 shows a flow sheet according to a combination of the processes of Fig. 2, Fig. 3 and Fig. 4 for 55 manufacturing titanium oxide.

Fig. 6 is a flow sheet which is basically the same as that of Fig. 4 except that a neutralization step for the titanium raffinate (c) is incorporated. In Fig. 6, the raffinate after titanium ion extraction is introduced to chloridization-oxidation step H, where at least one compound is added thereto which is selected from the

chlorides of Na, NH<sub>4</sub>, K, Ca, and Mg in an amount equivalent chemically to the total of free SO<sub>4</sub> ions and SO<sub>4</sub><sup>2-</sup> ions combined to Fe ions. The solution is then led to a chloride-complex-extraction step J, where it is brought into contact with an organic solvent (g) containing one or more of the species selected from the previously-defined oxygen-containing organic solvents, alkyl amines, and alkyl aryl amines, so that the Fe ions in the sulfuric acid solution are extracted as a chloride complex, giving a neutralized solution (k).

On the other hand, the Fe ions and the Cl ions extracted into the organic phase are brought into contact with water (j), in the inverse extraction step L to be inversely extracted into the aqueous solution, giving an iron-chloride-containing solution M and simultaneously regenerating the organic solvent (g).

In the case where an oxidizing agent containing NO<sub>3</sub> such as HNO<sub>3</sub>, NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, and the like is employed in the chloridization-oxidation step H, HNO<sub>3</sub> is extracted in the extraction step J together with the Fe ions and the Cl ions. The organic solvent containing the co-extracted HNO<sub>3</sub> is recovered in washing step K for selective removal of HNO<sub>3</sub> by contact with an aqueous solution containing one or more of the species selected from the compounds of Na and Cl; Mg and Cl; K and Cl; NH<sub>4</sub> and Cl; and Fe and Cl, transferring HNO<sub>3</sub> from the organic phase to the aqueous solution which is recycled to chloridization-oxidation step, whereby the substances contained therein such as NaCl and HNO<sub>3</sub> are reused. The process of Fig. 6 is also an advantageous method for manufacturing titanium oxide.

Fig. 7 shows a flow sheet basically the same as that of Fig. 4. Fig. 7 shows the advantage of the present invention in treating the sulfuric acid solution from which titanium is extracted off in the extraction step B. In this process, the raffinate is introduced to an evaporation-concentration step N operated under a reduced or normal pressure to decrease the volume of metal sulfate P discharged when a high concentration of sulfuric acid (m) is recovered for recycle, which is advantageous in manufacturing titanium oxide.

Fig. 8 shows a flow sheet of a method for manufacturing titanium oxides which is basically the same as that of Fig. 7. In the process of Fig. 8, titanium hydroxide G' is recovered from a titanium-containing aqueous solution (d) at a concentration step N' prior to the recycle, to the hydrolysis step E, of the aqueous solution (d) containing titanium inversely extracted from the organic phase at the inverse extraction step C by bringing the organic solvent (a) containing extracted titanium into contact with water, a dilute aqueous sulfuric acid solution or a reducing-agent-containing inverse extraction liquid, and then it is recycled to the hydrolysis step E.

Fig. 9 shows a flow sheet of a method for manufacturing titanium oxide which is basically the same as that of Fig. 7. In the process of Fig. 9, the concentrated sulfuric acid (m) derived from the evaporation-concentration step N operated under a reduced or ordinary pressure is recycled to the sulfation step R where the concentrated sulfuric acid is mixed with titanium-iron ore (Ilmenite or anatase) or titanium-concentrated slag Q to change the titanium in the raw material into titanyl sulfate. The mixture is subsequently leached at a leaching step S where titanyl sulfate solution A containing much impurity is derived by use of water or inverse-extraction liquid (d).

Fig. 10 shows a flow sheet of a method for manufacturing titanium oxide which is basically the same as that of Fig. 4. In the method of Fig. 10, the aqueous solution (d) resulting from the inverse extraction of titanium by contact of the organic solvent (a) containing extracted titanium with water or dilute sulfuric acid (b) inversely to extract titanium to the aqueous phase is introduced to a neutralization step T, where an alkali (n) is added to give titanium hydroxide G" having excellent adsorbing property.

Fig. 11 shows a flow sheet of an advantageous method of manufacture of titanium oxide which is basically the same as that of Fig. 6. In the process of Fig. 11, the aqueous sulfuric acid solution containing titanium and impurity ions which is obtained by addition of water (q) conventionally in hydrolysis step E and filtration of the resulting titanium hydroxide in the filtration step F is led to a chloridization step W for titanium, where a substance (f) is added which is selected from the compounds of Na and Cl; Mg and Cl; NH<sub>4</sub> and Cl; K and Cl; and HCl in an amount equivalent chemically to the chlorine sufficient for forming chloride of titanium contained in the sulfuric acid solution. The solution is subsequently led to the extraction step B where the titanium in the sulfuric acid solution is extracted in a form of a chloride complex by contact with organic solvent (a) containing an extractant selected from the previously-defined oxygen-containing organic solvents, alkyl amines, and alkyl aryl amines. Further, in the subsequent inverse extraction step C, the Ti ions and Cl ions in the organic phase is inversely extracted by contact with water (b) into the aqueous phase. The resulting aqueous solution (d') is introduced to a neutralization step T where alkali (n) is added to give titanium hydroxide G"

The various aspects of the methods of the invention are also illustrated by the following specific Examples.

## Example 1

The composition of the starting liquid for the experiment is shown in Table 1.

5

Table 1: Starting Solution for  $TiOSO_4$  Extraction

(Unit: g/l)

10	Total $H_2SO_4$	Total HCl	Ti	Fe	Zn	Mn	Al
15	401.1	<0.1	4.99	51.4	0.18	8.1	0.2

The extracting agents used in the comparative experiments for extraction are selected from alkyl-phosphine oxides and alkylamines.

20

Table 2: Comparison of Raffinate

(Unit: g/l)

25	Extracting Agent	Total $H_2SO_4$	Ti	Fe	Zn	Mn	Al
30	20 % Primen JMT	380.4	<0.01	51.4	0.17	8.1	0.2
35	15 % LA-1	391.6	2.21	51.4	0.18	8.1	0.2
40	10 % Alamine 336	401.1	4.98	51.4	0.18	8.1	0.2
	10 % Aliquat 336	400.3	4.52	51.4	0.18	8.1	0.2
	30 % TOPO	380.6	<0.01	51.4	0.18	8.1	0.2

45

The inverse extraction tests were conducted by employing the two extracting agents which had extracted titanyl sulfate more effectively, namely the primary amine (Primen JMT) and trioctylphosphine oxide (TOPO).

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Table 3: Inverse Extraction Test

(Unit: g/l)

Organic Solvent	Inverse Extracting Agent	Ti Concentration		
		Before Extraction	After Extraction	O/A
20 % Primen JMT + Kerosine	Water	8.1	1.1	1/5
30 % TOPO + Paraffin	Water	9.98	<0.1	1/5

## Example 2

NaCl was added to the starting solution shown in Table 1, and was used for the starting solution in this example.

Table 4: Test for Extraction of Chloride Complex

(Unit: g/l)

	Total H <sub>2</sub> SO <sub>4</sub>	Total HCl	Ti	Fe	Zn	Mn	Si
Starting Solution for Extraction	220.2	8.2	2.74	28.2	0.1	4.4	1.2
Organic Phase 30 % TOPO (after extraction)	1.1	12.1	5.48	2.04	0.2	<0.01	2.5
Organic Phase 20 % Primen (after extraction)	1.8	11.9	5.6	1.60	0.2	<0.01	2.5

## Example 3

The organic solvent used for the test contained 30 % TOPO and titanyl sulfate which had been brought therein by preliminary extraction. The Ti concentration in the organic phase was 12.4 g/l. The inverse extracting agent used was water containing 0.5 g/l of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>. O/A was 1/1, and shaking was conducted for 10 minutes.

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The Ti concentration in the organic phase after the inverse extraction was not more than 0.1 g/l. The color of the aqueous solution turned reddish violet, which shows the existence of  $Ti^{3+}$  ion therein.

Example 4

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The starting solution shown in Table 1 was used in this example. The organic solvents used contained TOPO (trioctylphosphine oxide) or THPO (trihexylphosphine oxide) as alkylphosphine oxides in an amount of 25 %.

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Table 5: Extraction of Titanyl Sulfate

(Unit: g/l)

15

	Total $H_2SO_4$	Ti	Fe	Zn	Mn	Cr	Mg
20	25 % THPO (Organic Phase) Raffinate (Aqueous Phase)	15.4	3.78	<0.01	<0.01	<0.01	<0.01
25	25 % TOPO (Organic Phase) Raffinate (Aqueous Phase)	16.8	4.11	<0.01	<0.01	<0.01	-

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The inverse extraction test was conducted with the organic solvents containing extracted  $TiO(SO_4)_2$  shown in Table 5.

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Table 6: Inverse Extraction of Titanyl Sulfate

(Unit: g/l)

Inverse Extracting Agent	O/A	Extracting Agent	Initial Ti	Ti after Equilibrium	Ti in Aqueous Phase
Water	1/2	TOPO	4.11	1.39	1.36
20 g/l $H_2SO_4$	1/2	TOPO	4.11	0.47	1.82
40 g/l $H_2SO_4$	1/2	TOPO	4.11	0.19	1.96
100 g/l $H_2SO_4$ + $C_6H_8O_6$	4/1	TOPO	4.11	0.89	12.86
Water	1/2	THPO	3.78	0.52	1.63
20 g/l $H_2SO_4$	1/2	THPO	3.78	1.18	1.30
40 g/l $H_2SO_4$	1/2	THPO	3.78	0.12	3.66
100 g/l $H_2SO_4$ + $C_6H_8O_6$	4/1	THPO	3.78	0.56	12.88

## Example 5

A continuous extraction test was conducted by use of an organic solvent containing 25 % TOPO, and the starting solution shown in Table 1. The extraction conditions were: O/A = 1/1, and 4-stage extraction.

Table 7: Continuous Extraction Test

(Unit: g/l)

Phase	Total $H_2SO_4$	Ti	Fe	Mn	Cr	Zn
Organic Phase (Outlet)	18.4	4.98	<0.01	<0.01	<0.01	<0.01
Aqueous Phase (Outlet)	382.7	<0.01	51.4	8.1	0.05	0.18

Continuous inverse extraction tests were conducted with the organic solvents containing the extracted titanyl sulfate shown in Table 7. The conditions were: 6-stage inverse extraction, at room temperature. The results are shown in Table 8.

Table 8: Continuous Inverse Extraction Tests

(Unit: g/l)

		Total $H_2SO_4$	Ti	Fe	Mn	Zn
10	25 % THPO + Kerosine	Organic Phase (Outlet)	<0.01	0.11	<0.01	<0.01
	5 g/l $H_2SO_4$	Aqueous Phase (Outlet)	45.1	9.96	0.15	<0.01
15	25 % TOPO + Paraffin	Organic Phase (Outlet)	<0.01	0.06	<0.01	<0.01
	40 g/l $H_2SO_4$ + $C_6H_8O_6$	Aqueous Phase (Outlet)	130.7	19.9	0.2	<0.01

## Example 6

25 Organic solvents containing extracted titanyl sulfate were brought into contact with a reducing gas, and thereafter brought into contact with water or dilute sulfuric acid for inverse extraction of titanyl sulfate to the aqueous phase. The results are shown in Table 9. Two organic solvents were used. The organic solvent (A) is paraffin containing 30 % TOPO and contains 4.11 g/l of extracted Ti; the organic solvent (B) is kerosine containing 25 % THPO and contains 3.78 g/l of extracted Ti.

Table 9: Reductive Inverse Extraction

(Unit: g/l)

Extracting Agent	Reducing Agent	Pressure	O/A	Inverse Extracting Agent	Equilibrium	
					Organic Phase	Aqueous Phase
TOPO	$H_2S$ Gas	5 kg/cm <sup>2</sup>	1/1	20 g/l $H_2SO_4$	0.02	4.09
THPO	$H_2$ Gas	4 kg/cm <sup>2</sup>	1/1	Water	0.32	3.48

## 50 Example 7

(Preparation of titanyl sulfate solution)

Ilmenite was used as the starting material which has the chemical composition of  $TiO_2$ : 44.2 %,  $FeO$ : 34.1 %,  $Fe_2O_3$ : 12.7 %,  $MnO$ : 0.3 %,  $Cr_2O_3$ : 0.01 %,  $V_2O_5$ : 0.15 %,  $P_2O_5$ : 0.03 %,  $Al_2O_3$ : 1.2 %,  $CaO$ : 0.25 %,  $MgO$ : 4.72 %, and  $SiO_2$ : 3.1 %. 2.7 kg of the ilmenite was pulverized to give a particle size such that 90 % thereof passes through -325 mesh sieve. The pulverized material was mixed with 4.5 kg of 95.1 %  $H_2SO_4$ , and preheated to a temperature of 80 °C.

A small amount of water was added thereto to promote sulfation reaction. The temperature of the mixture rose to 210 °C. After aging in that state for 5 hours, it was put into a liquid shown in Table 8 containing inversely extracted titanyl sulfate to dissolve the titanyl sulfate formed above. Since the reducing agent had been added to the liquid at the inverse extraction conducted before, the Fe ion was confirmed to 5 exist all as ferrous sulfate.

Insoluble residue: 0.31 kg  
 Leaching liquid (titanyl sulfate solution): 5.31 liters  
 Composition of the leaching liquid: TiO<sub>2</sub>:1984 g/l, Fe:180 g/l, H<sub>2</sub>SO<sub>4</sub>:804.1 g/l  
 Subsequently the leaching solution was cooled to 10 °C to separate crystalline iron sulfate. The yield of 10 the resulting FeSO<sub>4</sub> · 7H<sub>2</sub>O was 3.6 kg.

The quantity and the composition of the liquid after the crystals were filtered off were as below.

Liquid Quantity	Total H <sub>2</sub> SO <sub>4</sub>	Fe	Ti
4.01 liters	649.2 g/l	74.9 g/l	266.4 g/l

#### (Hydrolysis test)

20 The hydrolysis test was conducted with the liquid having the above composition.  
 Firstly, 0.5 liter of the liquid shown in Table 8 (containing 45.1 g/l of total H<sub>2</sub>SO<sub>4</sub> and 9.96 g/l of Ti) which had been used for inverse extraction of titanyl sulfate was preheated to 95 °C, and thereto 4.0 liters of the solution of the titanyl sulfate was continuously added.

25 To the resulting solution sufficiently adjusted to a certain concentration and maintained at a temperature of 95 to 98 °C, 1.1 liters of a liquid having been completed an inverse extraction as shown in Table 8 heated to 95 °C was added. The liquid was heated to the boiling temperature. When formation of precipitate was observed the heating and agitation were stopped and the liquid was subjected to aging.

30 After 30 minutes, agitation was restarted, and the liquid was heated again to the boiling temperature, being kept in that state for 3 hours. Thereto, 1.5 liters of the aqueous solution (containing 45.1 g/l of total H<sub>2</sub>SO<sub>4</sub> and 9.96 g/l of Ti) having been used for the inverse extraction as shown in Table 8 was added. When the completion of the hydrolysis was confirmed, the agitation was stopped.

#### (Calcination)

35 The resultant insoluble titanium hydroxide was dehydrated, washed and further washed with an acid. It was mixed with 0.5 % by weight of K<sub>2</sub>SO<sub>4</sub>, 0.1 % by weight of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 0.1 % by weight of ZnSO<sub>4</sub>, and the mixture was calcined at 870 °C for 60 minutes.

40 The yield of TiO<sub>2</sub> was 1.06 kg. The recovery rate of TiO<sub>2</sub> from the dissolved titanyl sulfate solution was 100.9 %, with the complete recovery of TiO<sub>2</sub> supplied from the inverse extraction liquid.

The amount and the composition of the liquid after filtration of titanium hydroxide were as below:

Amount of Liquid	Total H <sub>2</sub> SO <sub>4</sub>	TiO <sub>2</sub>	Fe
6.51 liters	399.4 g/l	9.1 g/l	49.8 g/l

45 The value of 9.1 g/l for TiO<sub>2</sub> is normal for the remaining amount in the sulfuric acid solution after hydrolysis. This proves that all of the TiO<sub>2</sub> in the inverse extraction liquid employed for the hydrolysis converted to the product.

50 The experimental yield of 100.9 % from the titanyl leaching solution to the titanium oxide clearly shows the effect of the extraction recovery in comparison with the conventional values of 94 to 95 %.

#### Example 8

55 A test was made for selective removal of Fe ions and Zn ions, co-extracted with titanyl sulfate, from the organic phase by washing.

The organic solvent used in this experiment was the one containing 30 % TOPO shown in Table 4, containing 5.48 g/l of Ti, 2.04 g/l of Fe, and 0.2 g/l of Zn. The washing solution used was the one containing

250 g/l of total  $H_2SO_4$  and 44.1 g/l of Ti. The conditions of washing were: O/A of 15/1, 2-stage countercurrent contact, at a room temperature.

5

Table 10: Impurity Removal Test

(Unit: g/l)

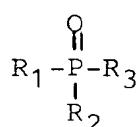
	Total $H_2SO_4$	Total HCl	Ti	Fe	Zn	Mn	Cr	Si
10								
15	Organic Phase (Outlet)	11.6	12.1	9.87	<0.01	<0.01	<0.01	2.46
20	Aqueous Phase (Outlet)	198.2	<0.1	22.15	30.6	3.01	<0.01	0.32

25

## Claims

1. A method for manufacturing titanium oxide from an aqueous sulfuric acid solution containing predominantly titanium ions and one or more other metal ions, which includes the steps of:
  - 30 a. subjecting said solution to hydrolysis to form insoluble titanium hydroxide;
  - b. separating the insoluble titanium hydroxide thus formed from the residual aqueous solution;
  - c. contacting the separated aqueous solution with a water-immiscible organic solvent consisting of or containing one or more oxygen-containing organic solvents, alkyl amines and/or alkyl aryl amines selected from:
    - 35 (i) a secondary amine represented by the general formula  $R_2NH$  where R is an alkyl or aryl radical having from 4 to 24 carbon atoms; and/or
    - (ii) a trialkylphosphine oxide represented by the general formula:

40

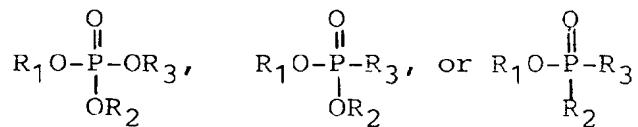


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(wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, each represents an alkyl or aryl radical having from 4 to 18 carbon atoms); and/or

(iii) a neutral alkyl phosphoric ester of general formula:

50

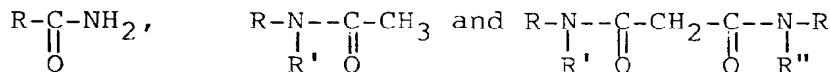


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(wherein  $R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, have the same meaning as above); and/or

(iv) a primary, secondary or tertiary alcohol having from 6 to 18 carbon atoms; and/or

(v) an amide of general formula:



(wherein R, R' and R'', which may be the same or different, each represents an alkyl or an aryl radical having from 4 to 22 carbon atoms);

so as thereby to extract still-dissolved titanium ions in the form of a sulfate titanyl complex into the organic solvent, and thereafter separating the resultant organic solvent extract from the aqueous raffinate;

d. contacting the separated organic solvent extract with water or dilute aqueous sulfuric acid solution to re-extract the titanium therefrom into the water or dilute aqueous sulfuric acid solution, thereby regenerating the organic solvent;

e. recycling the titanium-containing aqueous solution containing the re-extracted titanium back to hydrolysis step a.; and

f. calcining the separated titanium hydroxide from step b. to produce titanium oxide.

2. A method as claimed in claim 1, in which the water-immiscible organic solvent used in step c. includes one or more aromatic hydrocarbons, aliphatic hydrocarbons or mixtures thereof.

3. A method as claimed in claim 2, in which the organic solvent employed includes kerosene.

4. A method as claimed in any of the preceding claims, in which a reducing agent is added to the water or dilute aqueous sulfuric acid solution used in step d. prior to contact thereof with the separated organic solvent extract.

5. A method as claimed in any of the preceding claims, in which the separated organic solvent extract is first contacted with a reducing agent before it is contacted with the water or dilute aqueous sulfuric acid.

6. A method as claimed in claim 4 or claim 5, in which the reducing agent employed is one or more of the following, viz. H<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, Na<sub>2</sub>S, NaHS, NaC<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>C<sub>2</sub>O<sub>4</sub>, CH<sub>3</sub>COOH, CH<sub>3</sub>COONH<sub>4</sub>, CH<sub>3</sub>COONa, NaHSO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>HSO<sub>3</sub>, KHSO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, metallic iron, metallic zinc, hydrazine hydrate, hydrazine sulfate, citric acid, malic acid, gluconic acid, urea, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub> and/or ascorbic acid.

7. A method as claimed in any of claims 1 to 3, in which dilute aqueous sulfuric acid is employed in step d., without the use of any reducing agent, at a concentration of not more than 250 g H<sub>2</sub>SO<sub>4</sub> per liter.

8. A method as claimed in any of the previous claims, in which the titanium-containing solution from step d. is subjected to evaporation-concentration under a pressure no greater than atmospheric so as thereby to hydrolyze residual sulfate titanyl therein before the concentrated solution is recycled to hydrolysis step a.

9. A method as claimed in any of the previous claims, in which the aqueous raffinate from step c. is concentrated at a pressure no greater than atmospheric to recover concentrated sulfuric acid and decrease the quantity of sulfate titanyl therein.

10. A method as claimed in any of claims 1 to 7, which includes the subsequent steps of:

g. adding to the aqueous raffinate resulting from the step c. at least one Na, K, Mg, Ca and/or NH<sub>4</sub> chloride compound in an amount equivalent chemically to the sum of free SO<sub>4</sub><sup>2-</sup> ions and iron-bonded SO<sub>4</sub><sup>2-</sup> ions in the raffinate;

h. contacting the chloride-containing aqueous raffinate with a second water-immiscible organic solvent containing one or more oxygen-containing organic solvents, alkyl amines and/or alkyl aryl amines as claimed in claim 4 or claim 5, so as thereby to extract iron ions as a chloride complex from the raffinate into the second organic solvent, and thereafter separating the resultant second

organic solvent extract from the residual aqueous raffinate; and  
 i. contacting the second organic solvent extract with water to re-extract the iron ions and the chloride ions from the second organic solvent into the water, and thereby regenerate the second organic solvent.

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11. A method as claimed in claim 10, in which the chloride compound employed in step g. is rock salt (NaCl), NaClO<sub>x</sub>, seawater or an industrial waste containing such compounds, irrespective of purity.

10 12. A method as claimed in claim 10 or claim 11, in which the second organic solvent extract before re-extraction with water is first contacted with an aqueous solution containing at least one compound formed between Na and Cl, between Na and SO<sub>4</sub>, between Ti and Cl and/or between Ti and SO<sub>4</sub>, so as thereby selectively to eliminate impurities co-extracted with the chloride complex.

15 13. A method as claimed in any of the preceding claims, in which the hydrolysis of the sulfuric acid solution containing predominantly titanium ions and additionally one or more iron and/or other metal ions is effected by:  
 20 (i) adding H, Na, Mg, K, Ca and/or NH<sub>4</sub> chloride in the amount required to form a chloride complex of the titanium ion in the sulfuric acid solution;  
 25 (ii) contacting the complex-containing sulfuric acid solution with a third water-immiscible organic solvent containing at least one oxygen-containing organic solvent, alkyl amine and/or alkyl aryl amine as defined in claim 4 or claim 5, so as thereby to extract the titanium from the sulfuric acid solution in the form of a chloride complex;  
 (iii) contacting the third water-immiscible organic solvent extract with water so as thereby to re-extract the titanium ions and chloride ions from the organic solvent into the water, and thereby to regenerate the organic solvent, and thereafter separating the water from the regenerated organic solvent; and  
 (iv) neutralizing the separated water from step c. to precipitate titanium hydroxide, and separating the thus-precipitated titanium hydroxide.

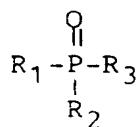
30 14. A method as claimed in any preceding claim, in which the chloride-complex-containing organic solvent extract or sulfate titanyl complex before re-extraction is first contacted with an aqueous solution containing at least one compound formed between Na and Cl, between Na and SO<sub>4</sub>, between Ti and Cl and/or between Ti and SO<sub>4</sub>, so as thus selectively to eliminate impurities co-extracted with the chloride complex of the titanium or sulfate titanyl complex.

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### Patentansprüche

1. Verfahren zur Herstellung von Titanoxid aus einer wäßrigen Schwefelsäurelösung, die überwiegend Titanionen und ein oder mehrere andere Metallionen enthält, einschließlich die Schritte:  
 40 a. Hydrolyse der Lösung, wobei unlösliches Titanhydroxid erzeugt wird;  
 b. Abtrennen des auf diese Weise erzeugten unlöslichen Titanhydroxids aus der zurückbleibenden wäßrigen Lösung;  
 45 c. in Kontakt bringen der abgetrennten wäßrigen Lösung mit einem mit Wasser nicht mischbaren organischen Lösungsmittel, bestehend aus oder enthaltend ein oder mehrere(n) Sauerstoff enthaltende(n) organische(n) Lösungsmittel(n), Alkylamine(n) und/oder Alkylarylamine(n), ausgewählt aus:  
 (i) einem sekundären Amin, wiedergegeben durch die allgemeine Formel R<sub>2</sub>NH, wobei R einen Alkyl- oder Arylrest mit 4 bis 24 Kohlenstoffatomen bedeutet; und/oder  
 (ii) einem Trialkylphosphinoxid, wiedergegeben durch die allgemeine Formel:

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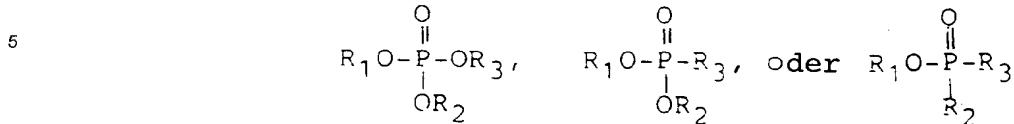


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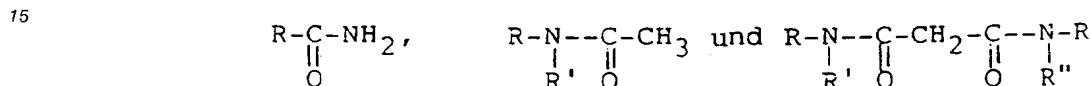
(wobei R<sub>1</sub>, R<sub>2</sub> und R<sub>3</sub>, die gleich oder verschieden sein können, jedes einen Alkyl- oder Arylrest

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mit 4 bis 18 Kohlenstoffatomen bedeutet); und/oder  
 (iii) einem neutralen Alkylphosphorsäureester der allgemeinen Formel:



10 (wobei  $\text{R}_1$ ,  $\text{R}_2$  und  $\text{R}_3$ , die gleich oder verschieden sein können, die gleiche, vorstehend angegebene Bedeutung besitzen); und/oder  
 (iv) einem primären, sekundären oder tertiären Alkohol mit 6 bis 18 Kohlenstoffatomen; und/oder  
 (v) einem Amid der allgemeinen Formel:



20 (wobei  $\text{R}$ ,  $\text{R}'$ ,  $\text{R}''$ , die gleich oder verschieden sein können, jedes einen Alkyl- oder einen Arylrest mit 4 bis 22 Kohlenstoffatomen bedeutet);  
 wobei dadurch noch gelöste Titanionen in Form eines Sulfattitanylkomplexes in das organische Lösungsmittel extrahiert werden, und danach Abtrennen des erhaltenen organischen Lösungsmittel-extraktes von dem wäßrigen Raffinat;  
 25 d. in Kontakt bringen des abgetrennten organischen Lösungsmittelextraktes mit Wasser oder einer verdünnten wäßrigen Schwefelsäurelösung, wobei das Titan daraus in das Wasser oder in die verdünnte wäßrige Schwefelsäurelösung zurückextrahiert wird, und dabei das organische Lösungsmittel regeneriert wird;  
 e. Zurückführen der Titan enthaltenden wäßrigen Lösung, die das zurückextrahierte Titan enthält, zu  
 30 dem Hydrolyseschritt a.; und  
 f. Kalzinieren des abgetrennten Titanhydroxids aus Schritt b., wobei Titanoxid hergestellt wird.

2. Verfahren nach Anspruch 1, wobei das im Schritt c. verwendete, in Wasser nicht mischbare, organische Lösungsmittel ein oder mehrere aromatische Kohlenwasserstoffe, aliphatische Kohlenwasserstoffe oder Gemische davon einschließt.
3. Verfahren nach Anspruch 2, wobei das angewendete organische Lösungsmittel Kerosin einschließt.
4. Verfahren nach einem der vorstehenden Ansprüche, wobei zu dem im Schritt d. verwendeten Wasser oder der verdünnten Schwefelsäurelösung vor seinem Kontakt mit dem abgetrennten organischen Lösungsmittelextrakt ein Reduktionsmittel zugegeben wird.
5. Verfahren nach einem der vorstehenden Ansprüche, wobei der abgetrennte organische Lösungsmittellextrakt, bevor er mit dem Wasser oder der verdünnten wäßrigen Schwefelsäure in Kontakt gebracht wird, zuerst mit einem Reduktionsmittel in Kontakt gebracht wird.
6. Verfahren nach Anspruch 4 oder Anspruch 5, wobei das angewendete Reduktionsmittel ein oder mehrere der nachstehenden Mittel, nämlich  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaHS}$ ,  $\text{NaC}_2\text{O}_4$ ,  $\text{NH}_4\text{C}_2\text{O}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONH}_4$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{NH}_4\text{HSO}_3$ ,  $\text{KHSO}_3$ ,  $(\text{NH}_4)_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{K}_2\text{S}_2\text{O}_3$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ , metallisches Eisen, metallisches Zink, Hydrazinhydrat, Hydrazinsulfat, Citronensäure, Äpfelsäure, Gluconsäure, Harnstoff,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{NH}_4\text{HCO}_3$  und/oder Ascorbinsäure bedeutet.
7. Verfahren nach einem der Ansprüche 1 bis 3, wobei im Schritt d. verdünnte wäßrige Schwefelsäure ohne die Verwendung eines Reduktionsmittels in einer Konzentration von nicht höher als 250g  $\text{H}_2\text{SO}_4$  pro Liter angewendet wird.

8. Verfahren nach einem der vorstehenden Ansprüche, wobei die Titan enthaltende Lösung des Schrittes d. unter einem Druck, der nicht höher als der Atmosphärendruck ist, dem Eindampfen-Konzentrieren unterworfen wird, wobei darin zurückgebliebene Sulfattitanylkomplexreste hydrolysiert werden, bevor die konzentrierte Lösung zum Hydrolyseschritt a. zurückgeführt wird.
- 5 9. Verfahren nach einem der vorstehenden Ansprüche, wobei das wäßrige Raffinat vom Schritt c. bei einem Druck, der nicht höher als der Atmosphärendruck ist, konzentriert wird, wobei konzentrierte Schwefelsäure wiedergewonnen und die Menge der Sulfattitanylkomplexverbindung verringert wird.
- 10 10. Verfahren nach einem der Ansprüche 1 bis 7, die folgenden Schritte einschließend:
  - g. Zugabe mindestens einer Na-, K-, Mg-, Ca- und/oder NH<sub>4</sub>-Chloridverbindung, zu dem wäßrigen Raffinat, das durch den Schritt c. erhalten wird, in einer chemisch äquivalenten Menge zur Summe der freien SO<sub>4</sub>-Ionen und der mit Eisen gebundenen SO<sub>4</sub>-Ionen in dem Raffinat;
  - 15 h. in Kontakt bringen des Chlorid enthaltenden wäßrigen Raffinats mit einem zweiten, mit Wasser nicht mischbaren, organischen Lösungsmittel, das ein oder mehrere Sauerstoff enthaltende organische Lösungsmittel, Alkylamine und/oder Alkylarylamine nach Anspruch 4 oder Anspruch 5 enthält, wobei Eisenionen als ein Chloridkomplex aus dem Raffinat in das zweite organische Lösungsmittel extrahiert werden, und danach Abtrennen des erhaltenen zweiten organischen Lösungsmittlextraktes von dem zurückgebliebenen wäßrigen Raffinat; und
  - 20 i. in Kontakt bringen des zweiten organischen Lösungsmittlextraktes mit Wasser, wobei die Eisenionen und die Chloridionen aus dem zweiten organischen Lösungsmittel zurück in das Wasser extrahiert werden, und wobei das zweite organische Lösungsmittel regeneriert wird.
11. Verfahren nach Anspruch 10, wobei die im Schritt g. angewendete Chloridverbindung Steinsalz (NaCl),  
25 NaClO<sub>x</sub>, Seewasser oder ein Industrieabwasser ist, das solche Verbindungen, unabhängig von der Reinheit, enthält.
12. Verfahren nach Anspruch 10 oder Anspruch 11, wobei der zweite organische Lösungsmittlextrakt vor der Reextraktion mit Wasser zuerst mit einer wäßrigen Lösung in Kontakt gebracht wird, die mindestens eine Verbindung enthält, die aus Na und Cl, aus Na und SO<sub>4</sub>, aus Ti und Cl und/oder aus Ti und SO<sub>4</sub> erzeugt wird, wobei dadurch Verunreinigungen, die mit dem Chloridkomplex zusammen extrahiert wurden, selektiv entfernt werden.
- 30 13. Verfahren nach einem der vorstehenden Ansprüche, wobei die Hydrolyse der Schwefelsäurelösung, die überwiegend Titanionen und außerdem ein oder mehrere Metallionen enthält, durch:
  - (i) Zugabe von H-, Na-, Mg-, K-, Ca-, und/oder NH<sub>4</sub>-Chlorid in einer Menge, die notwendig ist, einen Chloridkomplex des Titanions in der Schwefelsäurelösung zu erzeugen;
  - 40 (ii) in Kontakt bringen der den Komplex enthaltenden Schwefelsäurelösung mit einem dritten, mit Wasser nicht mischbaren, organischen Lösungsmittel, das mindestens ein Sauerstoff enthaltendes organisches Lösungsmittel, ein Alkylamin und/oder ein Alkylarylamin nach Anspruch 4 oder Anspruch 5 enthält, wobei das Titan aus der Schwefelsäurelösung in Form eines Chloridkomplexes extrahiert wird;
  - (iii) in Kontakt bringen des dritten, mit Wasser nicht mischbaren, organischen Lösungsmittlextraktes mit Wasser, wobei die Titanionen und die Chloridionen aus dem organischen Lösungsmittel zurück in das Wasser extrahiert werden, und dabei das organische Lösungsmittel regeneriert wird, und danach Abtrennen des Wassers von dem regenerierten organischen Lösungsmittel; und
  - (iv) Neutralisieren des abgetrennten Wassers des Schrittes c., wobei Titanhydroxid ausfällt, und Abtrennen des so ausgefallenen Titanhydroxids, durchgeführt wird.
- 50 14. Verfahren nach einem der vorstehenden Ansprüche, wobei der den Chloridkomplex enthaltende organische Lösungsmittlextrakt oder der Sulfattitanylkomplex vor der Reextraktion zuerst mit einer wäßrigen Lösung in Kontakt gebracht wird, die mindestens eine Verbindung enthält, die aus Na und Cl, Na und SO<sub>4</sub>, Ti und Cl und/oder aus Ti und SO<sub>4</sub> erzeugt wird, wobei auf diese Weise selektiv Verunreinigungen entfernt werden, die mit dem Chloridkomplex des Titans oder dem Sulfattitanylkomplex zusammen extrahiert wurden.

## Revendications

1. Procédé pour la fabrication d'oxyde de titane à partir d'une solution aqueuse d'acide sulfurique contenant essentiellement des ions titane et un ou plusieurs autres ions métalliques, qui comprend les étapes consistant à:

5 a. soumettre ladite solution à une hydrolyse pour former de l'hydroxyde de titane insoluble;

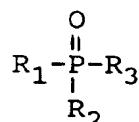
b. séparer l'hydroxyde de titane insoluble ainsi formé de la solution aqueuse résiduelle;

c. mettre en contact la solution aqueuse séparée avec un solvant organique non-miscible dans l'eau constitué de ou contenant un ou plusieurs solvants organiques contenant de l'oxygène, alkylamines et/ou alkylarylamines choisis parmi:

10 (i) une amine secondaire représentée par la formule générale  $R_2NH$  dans laquelle R est un radical alkyle ou aryle ayant de 4 à 24 atomes de carbone; et/ou

(ii) un oxyde de trialkylphosphine représenté par la formule générale:

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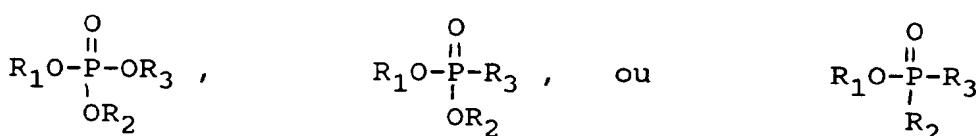


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(dans laquelle  $R_1$ ,  $R_2$  et  $R_3$ , qui peuvent être identiques ou différents, représentent chacun un radical alkyle ou aryle ayant de 4 à 18 atomes de carbone); et/ou

(iii) un ester alkylphosphorique neutre de formule générale:

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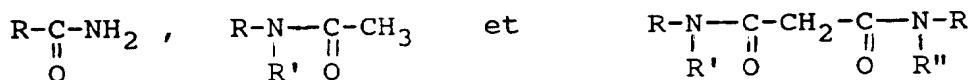
(dans lesquelles  $R_1$ ,  $R_2$  et  $R_3$ , qui peuvent être identiques ou différents, ont la même signification que précédemment); et/ou

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(iv) un alcool primaire, secondaire ou tertiaire ayant de 6 à 18 atomes de carbone; et/ou

(v) un amide de formule générale:

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(dans lesquelles R, R' et R'', qui peuvent être identiques ou différents, représentent chacun un radical alkyle ou aryle ayant de 4 à 22 atomes de carbone);

pour extraire de cette façon les ions titane encore dissous dans le solvant organique sous la forme d'un complexe sulfate de titanyle, et ensuite séparer l'extrait de solvant organique résultant du produit raffiné aqueux;

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d. mettre en contact l'extrait de solvant organique séparé avec de l'eau ou une solution aqueuse diluée d'acide sulfurique pour réextraire le titane de celui-ci dans l'eau ou dans la solution aqueuse diluée d'acide sulfurique, régénérant de cette façon le solvant organique;

e. recycler la solution aqueuse contenant le titane qui contient le titane réextract dans l'étape a. d'hydrolyse; et

f. calciner l'hydroxyde de titane séparé dans l'étape b. pour produire l'oxyde de titane.

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2. Procédé selon la revendication 1, dans lequel le solvant organique non-miscible dans l'eau utilisé dans l'étape c. comprend un ou plusieurs hydrocarbures aromatiques, hydrocarbures aliphatiques ou un mélange de ceux-ci.

3. Procédé selon la revendication 2, dans lequel le solvant organique employé comprend le kérosome.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel un agent réducteur est ajouté à l'eau ou à la solution aqueuse diluée d'acide sulfurique utilisée dans l'étape d. avant de mettre celle-ci en contact avec l'extrait de solvant organique séparé.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'extrait de solvant organique séparé est d'abord mis en contact avec un agent réducteur avant d'être mis en contact avec l'eau ou l'acide sulfurique aqueux dilué.
- 10 6. Procédé selon la revendication 4 ou la revendication 5, dans lequel l'agent réducteur employé est un ou plusieurs des agents suivants, c'est-à-dire  $H_2$ ,  $CO$ ,  $CO_2$ ,  $SO_2$ ,  $H_2S$ ,  $Na_2S$ ,  $NaHS$ ,  $Na_2CO_4$ ,  $NH_4CO_4$ ,  $CH_3COOH$ ,  $CH_3COONH_4$ ,  $CH_3COONa$ ,  $NaHSO_3$ ,  $Na_2SO_3$ ,  $Na_2S_2O_4$ ,  $NH_4HSO_3$ ,  $KHSO_3$ ,  $(NH_4)_2SO_3$ ,  $Na_2S_2O_3$ ,  $K_2S_2O_3$ ,  $(NH_4)_2S_2O_3$ , fer métallique, zinc métallique, hydrate d'hydrazine, sulfate d'hydrazine, acide citrique, acide maléique, acide gluconique, urée,  $(NH_4)_2CO_3$ ,  $NH_4HCO_3$  et/ou acide ascorbique.
- 20 7. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel l'acide sulfurique aqueux dilué est employé dans l'étape d. sans utiliser aucun agent réducteur, à une concentration qui n'est pas supérieure à 250 g de  $H_2SO_4$  par litre.
- 25 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la solution contenant le titane de l'étape d. est soumise à une concentration par évaporation sous une pression qui n'est pas supérieure à la pression atmosphérique, de façon à hydrolyser ainsi le sulfate de titanyle résiduel dans celle-ci avant que la solution concentrée soit recyclée dans l'étape a. d'hydrolyse.
- 30 9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le produit raffiné aqueux de l'étape c. est concentré à une pression qui n'est pas supérieure à la pression atmosphérique pour récupérer l'acide sulfurique concentré et diminuer la quantité de sulfate de titanyle dans celui-ci.
10. Procédé selon l'une quelconque des revendications 1 à 7, qui comprend les étapes complémentaires consistant à:
  - g. ajouter au produit raffiné aqueux résultant de l'étape c. au moins un composé de chlorure de Na, K, Mg, Ca et/ou  $NH_4$  dans une quantité chimiquement équivalente à la somme des ions  $SO_4$  libres et des ions  $SO_4$  liés au fer dans le produit raffiné;
  - 35 h. mettre en contact le produit raffiné aqueux contenant le chlorure avec un second solvant organique non-miscible dans l'eau contenant un ou plusieurs solvants organiques contenant de l'oxygène, alkylamines et/ou alkylarylamines tels que revendiqués dans la revendication 4 ou la revendication 5, pour extraire ainsi les ions fer en tant que complexe de chlorure du produit raffiné dans le second solvant organique, et ensuite séparer le second extrait de solvant organique résultant du produit raffiné aqueux résiduel; et
  - 40 i. mettre en contact le second extrait de solvant organique avec de l'eau pour réextraire les ions fer et les ions chlorure du second solvant organique dans l'eau, et régénérer ainsi le second solvant organique.
- 45 11. Procédé selon la revendication 10, dans lequel le composé de chlorure employé dans l'étape g. est du sel gemme ( $NaCl$ ),  $NaClO_x$ , de l'eau de mer ou un déchet industriel contenant de tels composés, sans tenir compte de la pureté.
- 50 12. Procédé selon la revendication 10 ou la revendication 11, dans lequel le second extrait de solvant organique avant la réextraction avec de l'eau est d'abord mis en contact avec une solution aqueuse contenant au moins un composé formé entre Na et Cl, entre Na et  $SO_4$ , entre Ti et Cl et/ou entre Ti et  $SO_4$ , pour éliminer ainsi sélectivement des impuretés co-extraiites avec le complexe de chlorure.
- 55 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'hydrolyse de la solution d'acide sulfurique contenant principalement des ions titane et en plus un ou plusieurs ions métalliques de fer et/ou d'un autre métal est effectuée par:

5 (i) addition de chlorure de H, Na, Mg, K, Ca et/ou NH<sub>4</sub> dans la quantité requise pour former un complexe de chlorure avec le ion titane dans la solution d'acide sulfurique;

(ii) mise en contact de la solution d'acide sulfurique contenant le complexe avec un troisième solvant organique non-miscible dans l'eau contenant au moins un solvant organique contenant de l'oxygène, une alkylamine et/ou une alkylarylamine telle que définie dans la revendication 4 ou la revendication 5, pour extraire ainsi le titane de la solution d'acide sulfurique sous la forme d'un complexe de chlorure;

10 (iii) mise en contact du troisième extrait de solvant organique non-miscible dans l'eau avec de l'eau pour réextraire ainsi les ions titane et les ions chlorure du solvant organique dans l'eau, et pour régénérer ainsi le solvant organique, et ensuite séparer l'eau du solvant organique régénéré; et

(iv) neutralisation de l'eau séparée à partir de l'étape c. pour précipiter l'hydroxyde de titane, et séparer l'hydroxyde de titane ainsi précipité.

15 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'extrait de solvant organique contenant le complexe de chlorure ou le complexe sulfate de titanyle avant la réextraction est d'abord mis en contact avec une solution aqueuse contenant au moins un composé formé entre Na et Cl, entre Na et SO<sub>4</sub>, entre Ti et Cl et/ou entre Ti et SO<sub>4</sub>, pour éliminer ainsi sélectivement des impuretés co-extraites avec le complexe de chlorure du titane ou complexe sulfate de titanyle.

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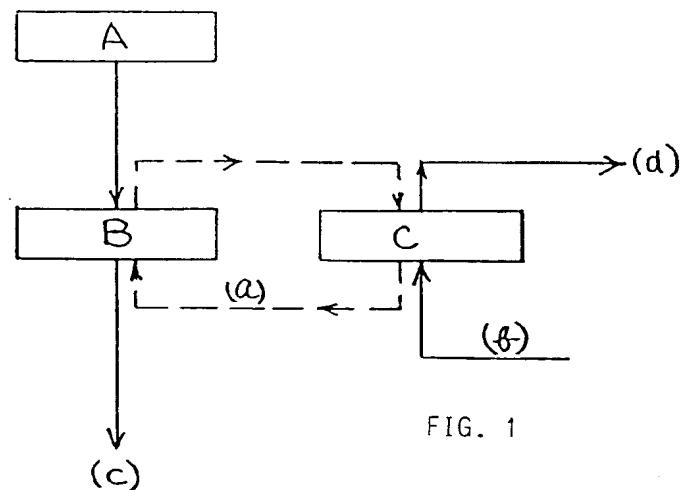


FIG. 1

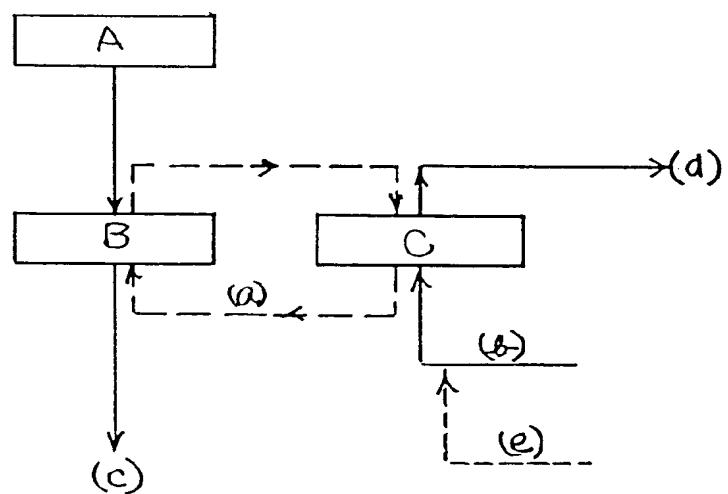


FIG. 2

FIG. 3

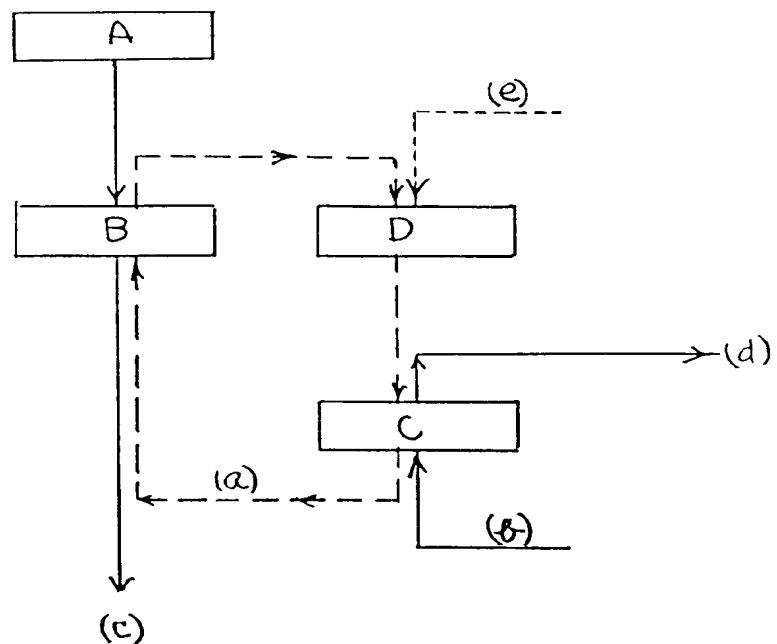
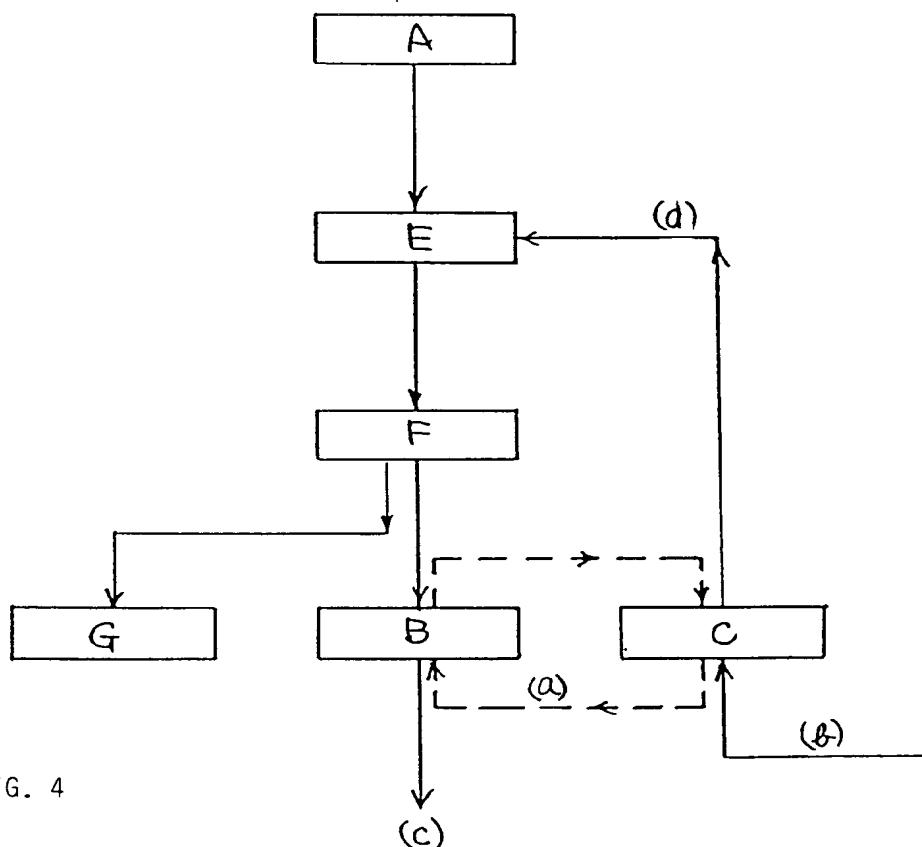


FIG. 4



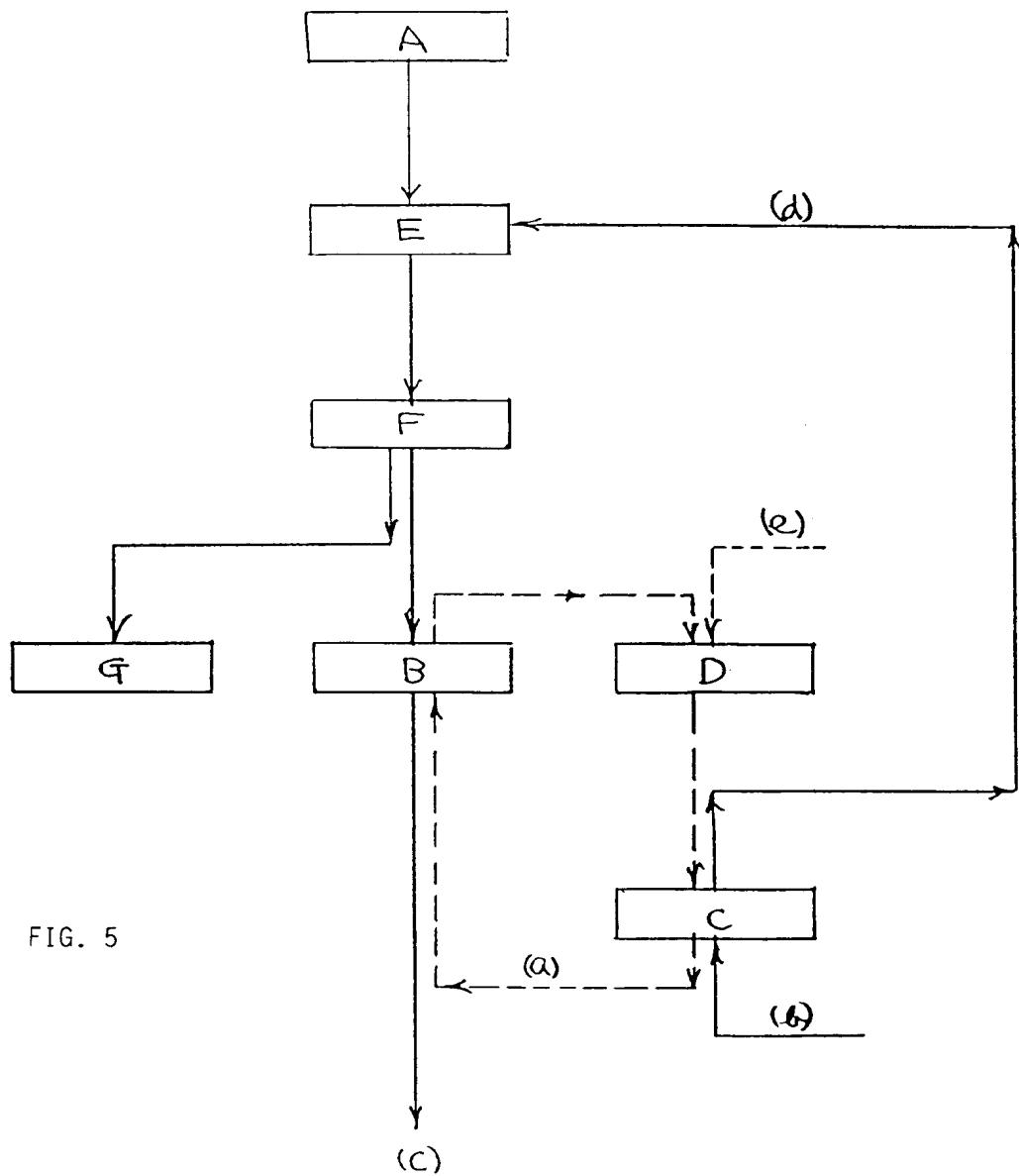


FIG. 5

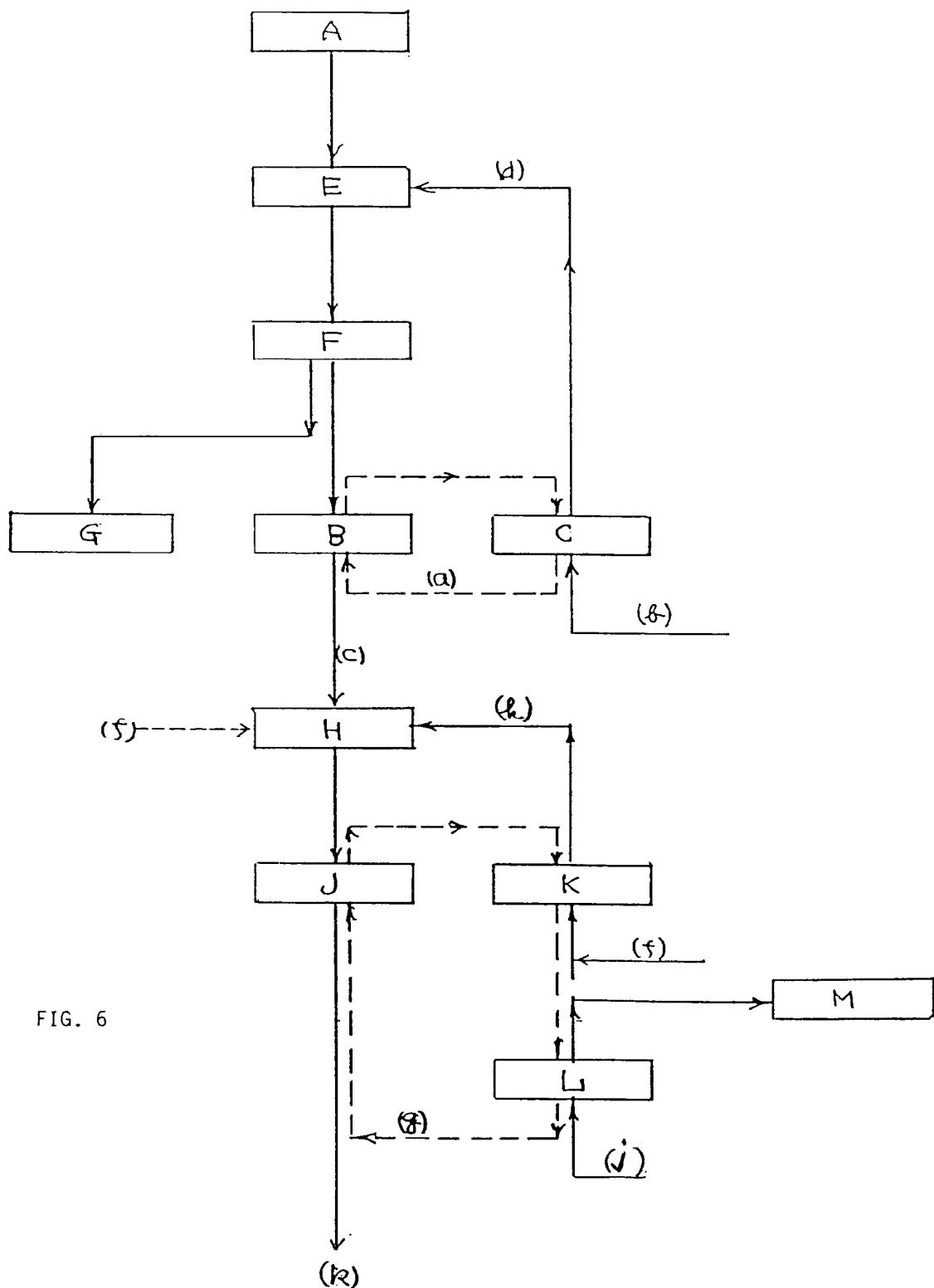


FIG. 6

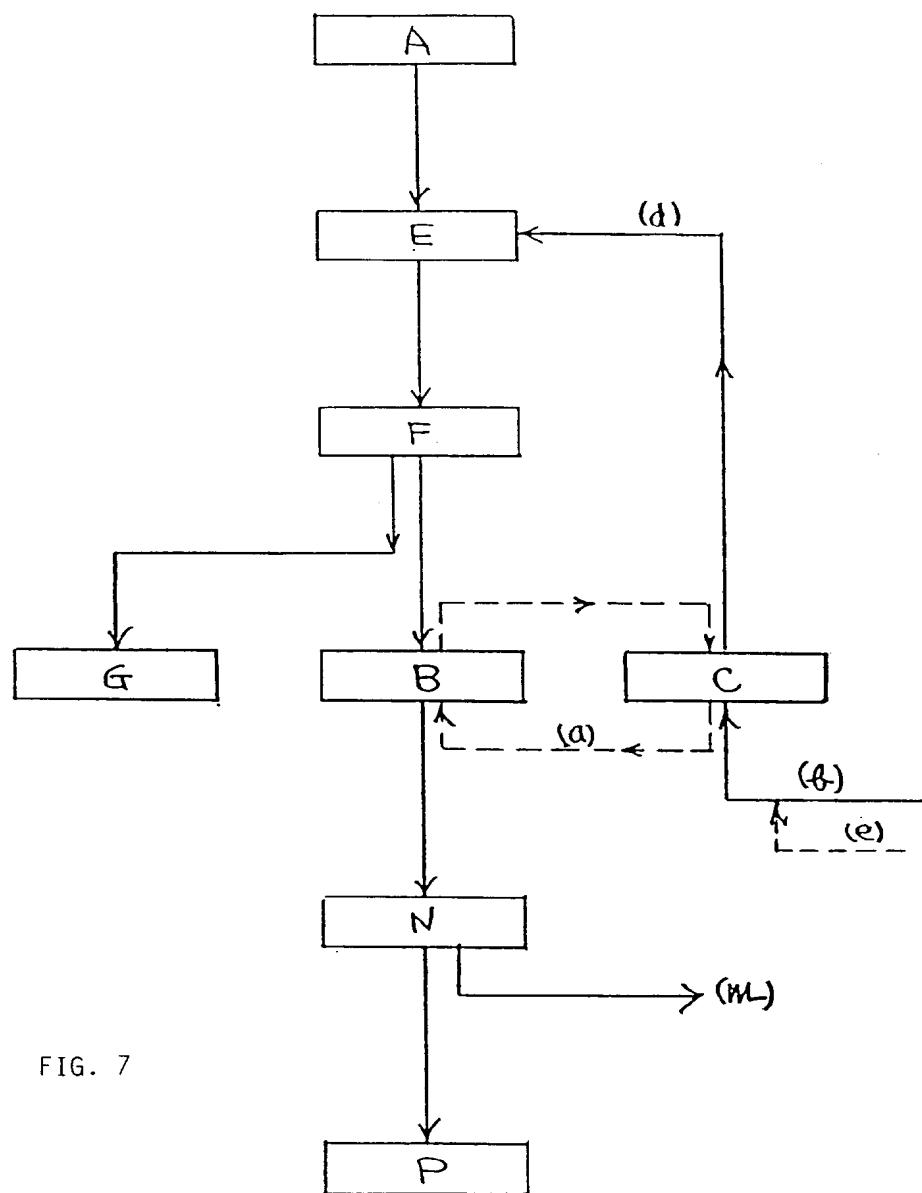


FIG. 7

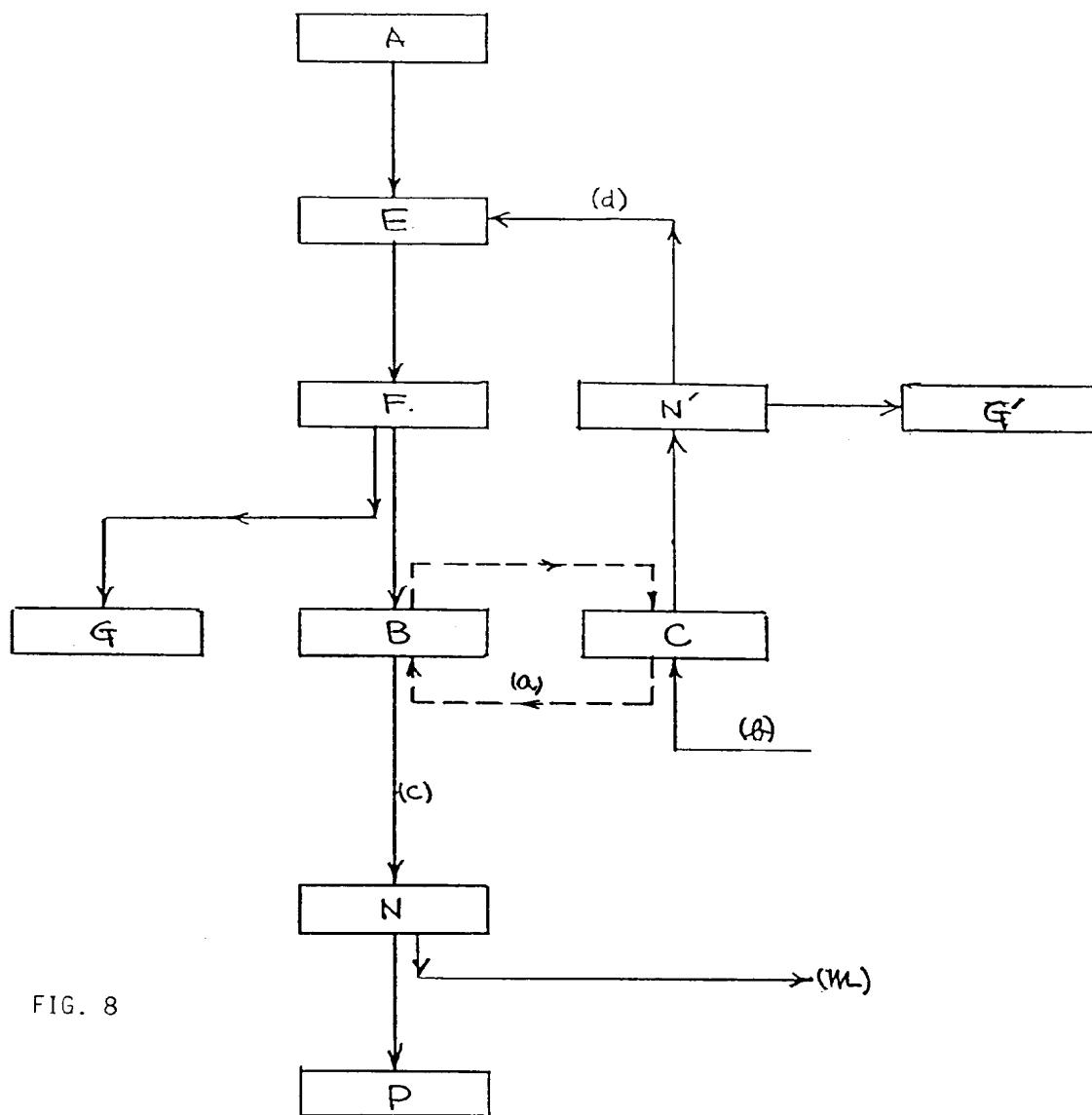


FIG. 8

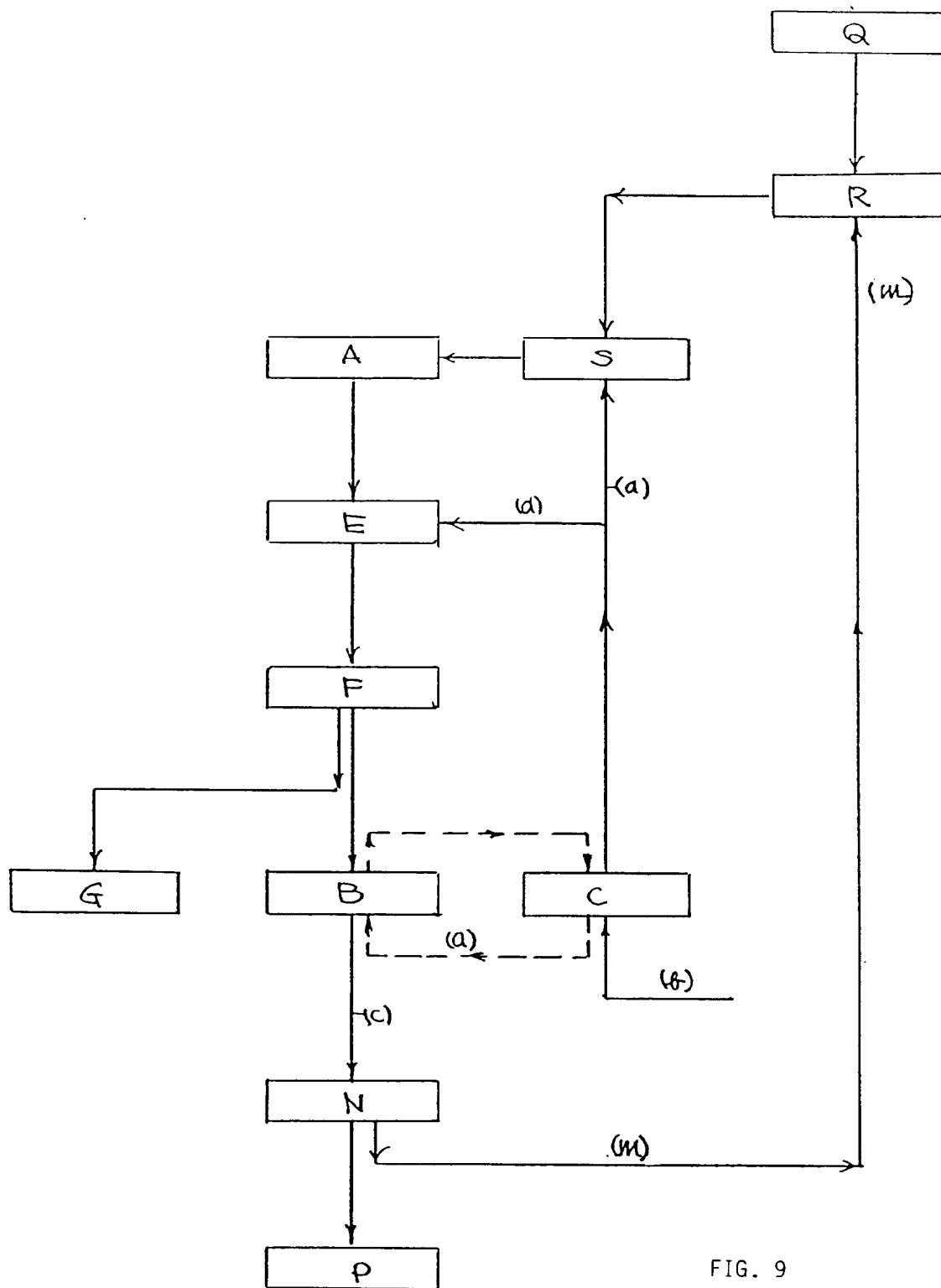


FIG. 9

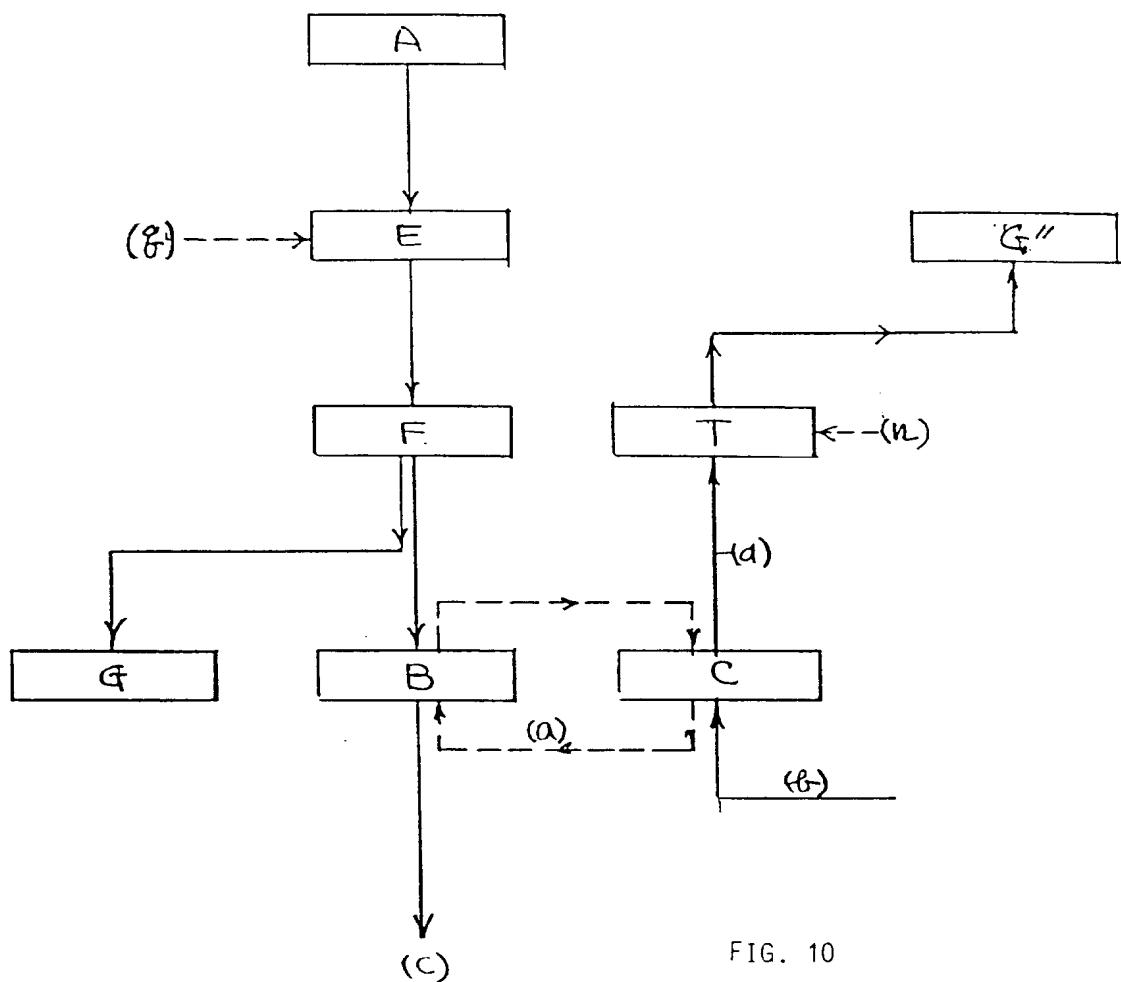


FIG. 10

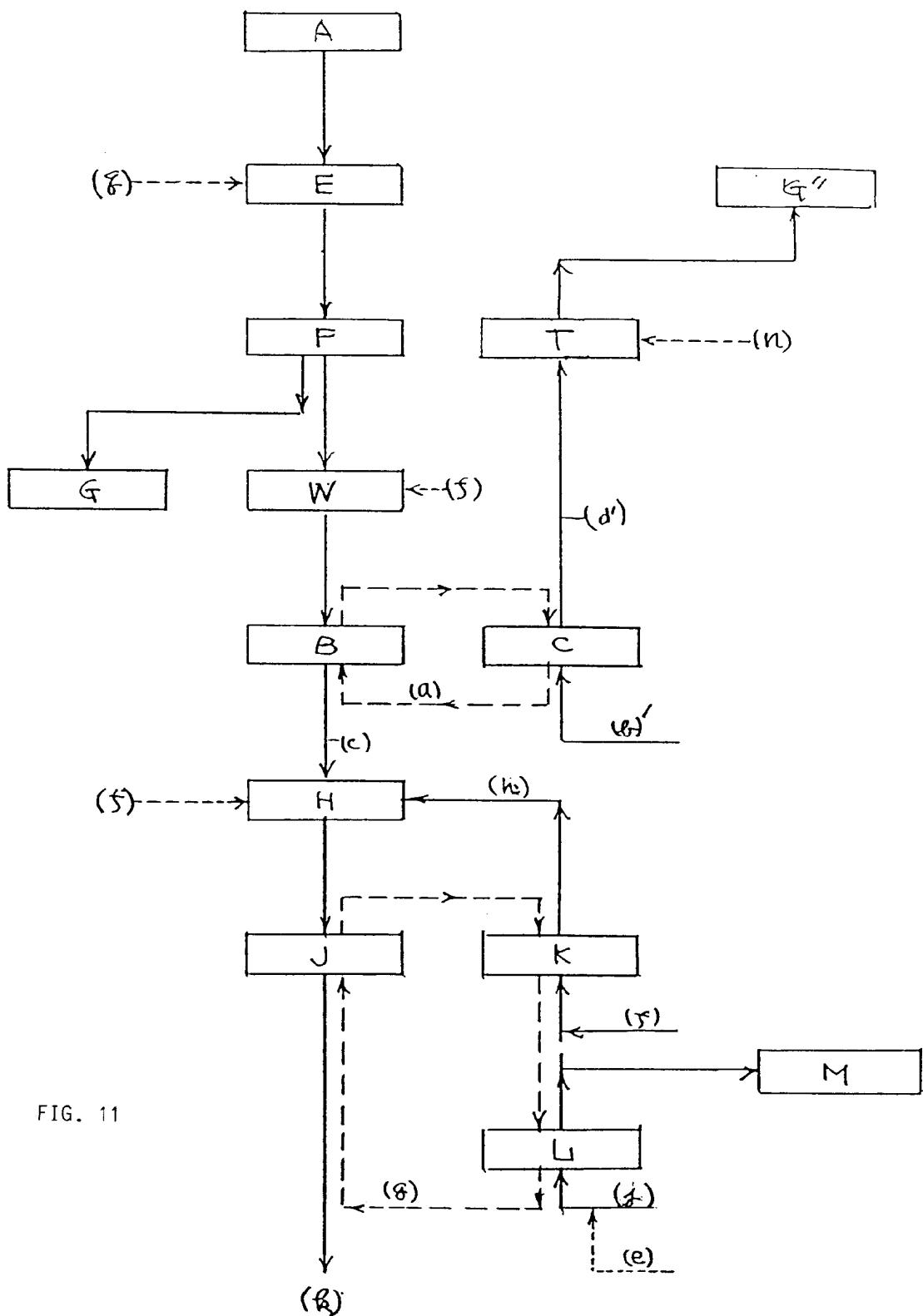


FIG. 11